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RP446

A METHOD FOR DETERMINING THE MOST FAVORABLE DESIGN OF GAS BURNERS

By John H. Eiseman, Elmer R. Weaver, and Francis A. Smith

ABSTRACT

The conditions which limit the satisfactory operation of a gas burner in its relation to the appliance are briefly discussed in a general way. Definite limits may be determined which show the conditions under which the flames flash back or blow from the ports and those under which combustion is rendered incomplete or "carbonizing" flames are produced. The relationships between these limiting conditions and several of the more important details of design and adjustment of the appliance are shown for the typical case of the top burner of a gas range burning a carbureted water gas of 570 Btu. The effects of the more important possible changes on the efficiency and rapidity with which heat is transferred are also shown, and the most favorable combination of conditions is systematically developed. The effects of the allowances which must be made in design for anticipated variations of pressure and inaccuracy of adjustment are also shown.

An appendix describes the laboratory apparatus which has been developed for experimental work of the kind involved.

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I. INTRODUCTION

The design and adjustment of a burner to give the most satisfactory operation, even when the composition of the gas to be supplied to the appliance is known and constant, is a complex problem. The Bureau of Standards was called upon to solve such a problem in the particular case of the top burner of a gas range to be supplied with propane, and subsequently has repeated the study with range burners for pure butane and for carburetted water gas of about 570 Btu. per cubic foot.

Although the use of a burner is rarely restricted to operation with gas of a definite composition, it is useful to know the design which would be the best for each of several such gases in order to determine the design of a burner which is to be used within an approximately known range of composition and service conditions.

This paper gives a detailed description of the method by which the best design for a given gas can be determined. From such a study it is possible to select the design and adjustment of a burner which will give the most satisfactory performance. Such performance includes a consideration of the efficiency of heating, the time required, and the safety of operation. Another paper now being prepared will contain a report of the results obtained by applying this method of study to each of several gases, such as the three listed above, from which the best design of burner for each can be obtained.

1. LIMITS OF OPERATION OF AN APPLIANCE

A discussion of the conditions which limit the safe operation of an appliance, and their determination, is given in Bureau of Standards Technologic Paper No. 304, Method of Testing Gas Appliances to Determine Their Safety from Producing Carbon Monoxide. A portion of the discussion is repeated here because a thorough understanding of what these limits are and how they affect the operation of an appliance is absolutely essential to an understanding of the tests which follow.

Nearly all gas burners employed in domestic appliances are of the Bunsen or "blue flame" type and are commonly referred to as "atmospheric" burners. These burners are so designed that a portion of the air necessary for complete combustion mixes with the gas before it reaches the burner ports. This is called "primary" air. The additional air required is secured from the atmosphere surrounding the flames, and is termed "secondary" air. As the amount of primary air which mixes with a given amount of gas is increased, a limit is reached above which the flames either blow away from the ports or flash back into the burner, depending upon the gas rate used. Similarly, if the primary air is decreased, a limit is reached below which the color of the tip of the inner flame cone becomes yellow. This results from the formation of finely divided particles of solid carbon which do not burn nearly so readily as the gases from which they are formed.[1]

One of the principal requisites of a well designed appliance is that it be capable of burning completely the gas supplied to it, or stated

[1] For a more complete discussion of the principles underlying these three conditions, see B. S. Circular No. 394, pp. 3 to 8.

in another way, no incomplete combustion should result from any usual adjustment of gas or primary air.

A burner that is adjusted so that the flames are blowing away from the ports or have flashed back into the burner is not burning the gas completely. A flame having a yellow tip may also result in incomplete combustion and is objectionable in most cases because it may produce a carbon deposit on the material being heated.

Incomplete combustion may also result from other causes, such as inadequate combustion space, too little or improperly applied secondary air, etc., even when the burner is adjusted so that none of the other limits are encountered.

The quantitative determination and representation of these limits constitute the first part of the experimental work described in this paper. The application of the knowledge thus obtained to the problem of design is the next step.

Without doubt the limits of safe operation of an appliance are affected to some extent by barometric pressure. The results reported in this paper were obtained at sea level and should not be assumed to apply without modification to the operation of appliances at very high altitudes. The effect of altitude on the operation of appliances is a subject upon which future work is planned.

2. GENERAL PROCEDURE IN THE DESIGN OF AN APPLIANCE

A considerable portion of the field of burner design is covered in an elementary manner by Bureau of Standards Circular No. 394, entitled "Design of Gas Burners for Domestic Use." In that circular the various factors which affect a favorable design are pointed out, and their relationships are indicated in a qualitative manner. The method of investigation and analysis described in the present paper develops the important relationships quantitatively.

Because of the difficulty of making useful generalizations regarding the design of the many types of appliances in use, the discussion in Circular No. 394 was strictly limited to the burner itself to the exclusion of its environment, which was assumed to be predetermined. The present paper deals with the design of a burner for a specific application, "top burner" cooking, in which the utensils to be heated are supported by an open grate. The environment of the burner in this case is subject to one and only one important variation, the distance between the burner and the utensil heated. This paper therefore considers the position of the burner in addition to the design of the burner itself.

It is assumed in the discussion which follows that the reader is familiar with the fundamentals given in Circular No. 394, but for the reader who does not have access to the circular the necessary steps in designing a burner are again summarized in the approximate order in which they should be taken by quoting the summary of the circular.

Whether these steps can be followed in the exact order given depends upon which factors are known at the start. The order given assumes that nothing is known at first about the burner and that everything is known about the remainder of the appliance. There are many cases, however, in which some of the necessary characteristics of the burner may be known. For example, the proper size of port and the desired gas rate may be known, and if experience has shown that it is desirable to have a certain port area for this rate, then the number of ports and

approximately the minimum size of the burner head could be determined from these facts. It is important to give all of the various factors sufficient consideration irrespective of the order in which they are taken. The summary of Circular No. 394 follows:

1. Determine the general shape and size of the burner from the space available and the manner in which the heat is to be applied.

2. Determine the arrangement of ports and provide for the escape of products of combustion with a view to insuring a uniform flow of secondary air to and away from each port with as little excess as is needed.

3. Determine the number and size of ports, making the number as large as can be provided for without excessive cost, and choosing a size which will permit a maximum of primary air without danger of either back-firing or lifting. As a general rule, trouble from back-firing will be avoided with manufactured gas if ports are drilled with No. 40 drills or smaller. Propane and butane permit the use of No. 32 drills, natural gas the use of No. 30 drills. This rule is subject to modification because of the conditions of use of the burner. If it is always supplied with gas at a uniform high rate, if there is no advantage in using much primary air, and if the burner is but slightly heated during use, the size of the ports may be increased with advantage. Burners which require much primary air, which become very hot, and which are likely to be turned low, must have smaller ports. To avoid the lifting of the flames, burners for manufactured gas

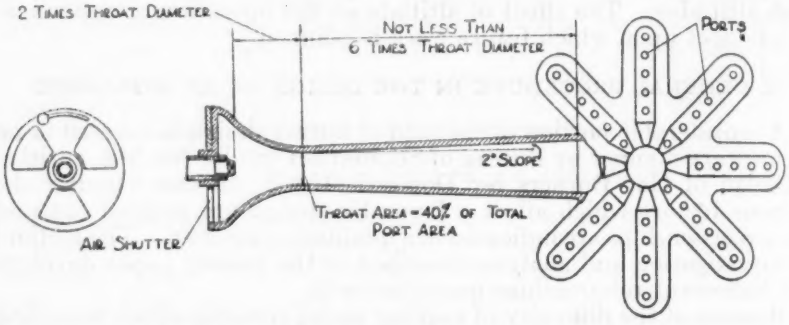

FIGURE 1.—*Relative dimensions of a domestic gas burner to attain the maximum entrainment of primary air*

should have at least 1 square inch of port area for each 25,000 Btu. per hour when gas is burned at the maximum rate. Burners for natural gas should have 1 square inch of port area per 10,000 Btu. per hour and burners for propane and butane 1 square inch per 12,000 Btu. per hour. These figures are subject to modification for the same reasons as are those for the size of ports.

4. Design the burner head of liberal size and with deep metal, through which the ports are machined.

5. Design the passages of the burner without abrupt changes in size or direction so that the stream of gas and air will expand gradually and approach the ports at low and uniform velocity. Make the area of the burner throat equal to about 40 per cent of the port area, and other dimensions of the mixer approximately as shown in Figure 1.

6. Select tentatively, for each of as many sets of conditions as seem necessary to cover the range of conditions in which the appliance is to be used, an orifice of area a, using the formula

$$q = 1{,}300\, a \sqrt{\frac{h}{d}}$$

where

q is the maximum desirable volume of gas in cubic feet per hour,
h is the maximum gas pressure in inches of water, and
d is the specific gravity of the gas referred to air.

7. Assume the desired ratio of primary air to total air required for complete combustion from experience or from the discussion in this paper.

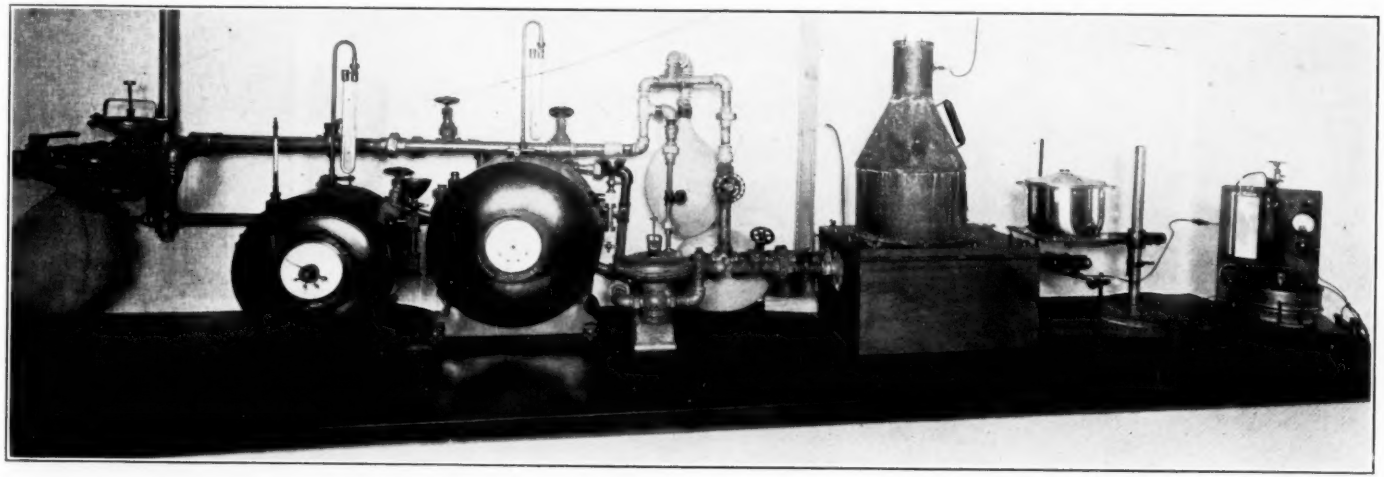

FIGURE 2.—*Apparatus used to study the performance of gas burners*

8. Assume a value for a burner constant k, from experience with a burner of the same general form or from the discussion in this paper (in the absence of any previous knowledge k may be tentatively assumed equal to $0.6\sqrt{P}$, where P is the total area of the ports) and compute whether the burner tentatively planned will entrain the desired amount of primary air under each set of conditions assumed as representative of those to be met. Use the formula

$$\frac{Q}{q} = k\sqrt{\frac{d}{aD}}$$

or one of its modifications given in the discussion. Q is the volume of primary mixture which flows per unit time, q is the volume of gas which flows per unit time, D is the specific gravity, referred to air, of the primary mixture, and a and d have the meanings stated in paragraph 6. The constant k is usually obtained by solving the same formula in which have been substituted values for the other symbols known from experience with a burner of similar form.

9. Having completed a model burner, determine by trial whether its performance is satisfactory within the range of air-shutter adjustment with respect to (1) completeness of combustion at the maximum rate of heat supply with the gas having the greatest requirement of "air for complete combustion," (2) back-firing with the most rapidly burning gas at minimum rate, and (3) lifting of the flames with the slowest burning gas at maximum rate.

10. Determine by trial the maximum primary air that will allow an ample factor of safety against unstable flames, and while using this high primary air place the burner or regulate secondary air to give as high efficiency as may be obtained while providing an ample factor of safety against incomplete combustion.

11. Select the orifice to be used with a particular gas supply by the aid of the formula given in paragraph 6, or a corresponding one for the type of orifice used, if the orifice is known to give a result different from that of the formula. Then employ the formula stated in paragraph 8, and a value of the burner constant k determined by observation on the model under conditions as nearly as possible like those of service, and determine that the entrainment of primary air will be satisfactory within the range of adjustment of the air shutter. If the air required for complete combustion of the future supply of gas is not known, assume that 9 cubic feet of air will be needed per 1,000 Btu.

It will be apparent at once to the reader that certain very important details have been left to the judgment of the designer or to be determined by trial. Among these are the exact size of the ports, the location of the burner with respect to the object to be heated, and the proportion of primary air to be used. The most favorable values for these various quantities are related to one another, and also to such considerations as complete combustion and the efficiency and speed of accomplishing a desired operation, in such a way that they can not be determined independently but must be evaluated as a group if the best result is to be obtained.

Information of this nature is not always available and in such cases it is necessary to obtain it by actual test. Indeed, the values suggested in Circular No. 394 for use in the preliminary design of an appliance were in large part selected from a consideration of the results of tests reported for the first time in the present paper. It is hoped that the detailed discussion which follows will not only make it possible for a designer to obtain such information when desired, but will also give him a better understanding of the effect of changing different variables on the operation of an appliance.

II. METHOD OF EXPERIMENTAL STUDY

1. SELECTION OF THE BURNER CASTING AND THE NUMBER OF PORTS

In order to make this discussion as clear as possible, a complete description of the method of test will be given as applied to a gas-range burner to be used with manufactured gas. However, the method is equally applicable to other gases or other types of appliances.

In this study it was required to design a "top burner" and make the most suitable adjustments of the burner for a gas range with open grate which was to be supplied with carburetted water gas of 570 Btu. per cubic foot.

The first step in design, the selection of the general size and shape of the burner head, was made somewhat arbitrarily. Past experience indicated that a star-shaped burner is superior to any other form employing drilled ports, for heating a utensil placed above it. A star burner permits secondary air to flow upward on both sides of every row of ports, and products of combustion to flow radially outward between rows of ports in a space that increases in width in proportion to the volume of the products. This arrangement results in a very favorable application of heat to the utensil, satisfactory aeration of the flame at each port, and a minimum of interference between secondary air and products of combustion, especially when the grate employed to support the utensil has the bars arranged radially. For these reasons a star burner was selected. The most favorable diameter for the burner, the number of its prongs, and the most favorable spacing of the ports may be made the subject of future investigation. These variables were not included in the present study because they were believed to be less important than several other factors which should be studied first and because their selection is dependent largely upon the cost of manufacture, which is not easily included in a quantitative way in a laboratory investigation. These considerations and the availability of a sufficient number of similar burner castings led to the choice for this work of an 8-prong star burner, 4½ inches in diameter and having 44 ports drilled in the manner shown in Figure 1. The castings met reasonably well the requirements of a good burner with respect to ability to entrain air and the distribution of pressure within the burner head.

2. DETERMINATION OF FLASH-BACK, BLOW-OFF, AND YELLOW-TIP LIMITS AND THE EFFECT OF VARYING THE PORT SIZE ON THESE LIMITS

The most desirable size of the ports is dependent upon the composition of the gas to be used, and to secure accurate information relative to the proper size for the given gas supply it was necessary to find quantitatively the effect of changes in port size on the position of the flash-back, blowing, and yellow-tip limits mentioned in the introduction. These limits are nearly independent of the position of the burner relative to the material heated. Efficiency, rate of heating, and the conditions under which combustion becomes incomplete are not thus independent, hence the conditions mentioned in the first group should be determined first, and the information obtained made use of to reduce the amount of work necessary in the study of the remaining conditions, as well as in the final selection of the most favorable combination.

In order to determine the conditions under which these three limits occur, the burner was installed so that both the gas rate and the supply of primary air could be varied at will. It was also essential to have suitable equipment for accurately controlling and measuring the rate of flow of both gas and air for each adjustment. Figure 2 shows the apparatus used for these tests.[2] Having the burner installed in such

[2] A detailed description of this apparatus is given in the Appendix. A brief discussion is also given in B. S. Tech. Paper No. 304.

an apparatus and burning gas at a constant rate, the primary air was increased until the flames either lifted from the ports or flashed back into the burner. When this condition was reached the relative proportion of air and gas was determined. The primary air was next decreased until yellow appeared in the flame, and the ratio of air to gas again determined. The gas rate was then changed and the same procedure repeated. This procedure was continued until a series of tests had been made which covered the desired range of gas rates. The results obtained were plotted, using as the coordinates "Gas rate: thousands of Btu. per hour per port" and "Primary air: per cent of total air required." [3]

Figure 3 represents the position of the boundaries of the regions in which flash back, blow-off or "lifting," and yellow tips occur in the

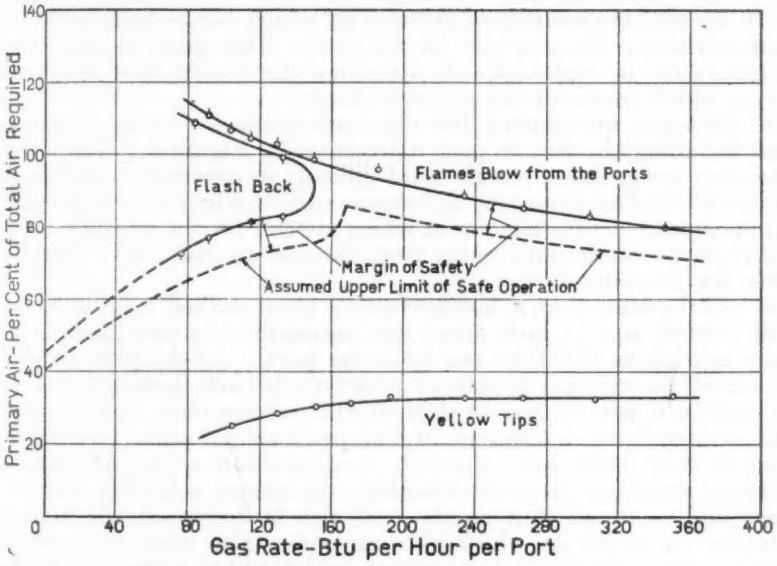

FIGURE 3.—*Boundaries of the regions in which flash back, lifting, and yellow tips occur*

Port size, No. 38. Carburetted water gas of 570 Btu. per cubic foot

case of ports drilled with a No. 38 (drill manufacturers' standard) twist drill (diameter, 0.1015 inch or 2.578 mm. Area, 0.0081 in.^{2} or 5.23 mm^2). The small circles with short lines pointing upward represent conditions under which the flames were observed to lift; those with short lines pointing downward represent conditions under which flash back was observed to occur; and circles without pointers represent the recorded appearance of yellow tips. Unfortunately, it is impossible with a multiple port burner and the experimental facilities used to determine the position of the flash-back curve at very low gas rates, but an unpublished study of flash back with a single-port burner under more accurately measurable conditions has established the shape of the flash-back curve, which is similar to the often

[3] The choice of "Btu. per port" as the abscissa permits the application of the results directly to a burner having a different number or arrangement of well-aerated ports. The ordinate selected permits the most convenient intercomparison of different gases, the full advantage of which appears only in other papers in which such comparisons are of particular importance.

published curves of flame velocity (usually rotated through an angle of 90°). The extrapolated portion of the curve is probably accurate enough for practical purposes, as will appear in connection with the discussion of Figure 5.

Since neither the flash back nor the lifting curve can be determined with absolute accuracy even under laboratory conditions, and still greater variations are encountered under conditions of use, it would be foolish to design an appliance to operate with exactly the highest air injection indicated by laboratory tests to be safe. It is therefore desirable to establish a margin of safety corresponding to the "factor of safety" usually assumed by engineers in designing mechanical structures. The margin of safety somewhat arbitrarily chosen is defined by reducing by 10 per cent the amount of primary air which causes the flames to lift at each gas rate and by similarly reducing by 10 per cent the amount of primary air which causes flash back, and then increasing the gas rate 10 per cent. This gives as the upper boundary of the region of safe operation the dotted lines below the curves which represent the observed limits.

In Figure 4 are plotted the observed limits for ports of several sizes including the No. 38 port represented in Figure 3. The curves bounding the yellow-tip region are difficult to determine, within the limits of variation caused by differences of port size, and are relatively unimportant. Only one curve, which represents the average of the observations made with ports from No. 38 to No. 44 is therefore given for this boundary.

It will be seen that a burner having ports drilled with a No. 36 drill (0.0089 square inch area) was susceptible to flash back at gas rates as high as 216 Btu. per hour per port. As the port size was decreased the maximum rate at which flash back occurred was depressed until with a No. 44 drill (0.0058 square inch area) no flash back occurred above a rate of 40 Btu. per hour per port. Obviously, then, if flash back were the only consideration a No. 44 port, or smaller, would be the most suitable. However, a further study of these curves shows that as the port size is decreased the ratio of primary air to gas at which blowing occurs also decreases and the problem is presented of selecting ports which will give the best results, considering both flash back and lifting. To solve this problem it is necessary to introduce certain facts, learned from experience, the verification of which will appear later in the paper.

It has been found that the highest efficiencies are possible if an appliance is designed to take the greatest amount of primary air that can be introduced without causing the flames either to lift or to flash back. Consider a burner that is supplied with both gas and primary air at constant rates, placed under a utensil that can be moved upward or downward at will. If the utensil is initially at a great distance from the burner there is no possibility that the utensil will interfere with the combustion of the gas, but very little of the heat produced by burning the gas will be transferred to the utensil; stated in another way, the "efficiency" will be very low. As the utensil is brought closer to the burner the efficiency increases, but a level is eventually reached at which the utensil does interfere with combusion, either through the effect of diminished temperature near its surface, or by preventing the access to the flames of enough secondary air, or both. If the utensil is left in the position at which incomplete combustion

first appears and the supply of primary air is increased, combustion again becomes complete. Incidentally, the efficiency is diminished by this addition of primary air, but only to a small extent. If the utensil is again lowered, efficiency again increases. When incomplete combustion is again encountered the efficiency is found to be higher than when combustion became incomplete with the smaller amount of primary air. The process may be repeated with a closer approach of utensil to burner and an increase of efficiency for every addition of primary air until either flash back or lifting prevents further progress in this manner.

Another series of related facts must now be considered. A range burner is not always operated at the same gas rate; the gas is frequently, if not usually, "turned down" for the heating of small utensils, for gentle boiling, and for some other cooking processes. The burner must be adjusted to operate satisfactorily over the entire range of useful rates of heating without change other than the manipulation of the gas cock. To ascertain what single adjustment will permit this, it is necessary to determine the amount of primary air injected into the burner by gas supplied at different rates under the conditions of practical or "normal" use. A curve which represents the amount of air thus entrained in a burner with fixed adjustments when only the supply of gas is varied is commonly called, "a normal air-injection curve." Such a curve is determined by analyzing the mixture of gas and air that enters the burner under conditions of normal use. For the results to be completely significant, the orifice through which the gas is delivered and the opening of the air shutter, as well as the details of construction of the burner must be definitely known. If the size, form, or position of the orifice, the opening of the air shutter, the size or number of the ports, or the form of the burner is changed, a different normal air-injection curve will be obtained. However, it is important to note that a change in one of these details of design or adjustment, such as the size of the ports, great enough to make a decided change in the position of the normal air-injection curve affects the shape of that curve very little or not at all. Hence, a change in another detail, such as the opening of the air shutter, can usually be made which will bring the curve back to the position it had before any change was made.

This fact makes it possible to determine a series of normal air-injection curves with one burner, and to use these curves to predict with satisfactory accuracy the effect, on the amount of air injected, of varying the supply of gas to a burner of somewhat different design. Each of the normal air-injection curves of the one burner can be reproduced with the other burner by making suitable adjustments of orifice and air shutter.

In Figure 4 the observed positions of flash-back and lifting curves were shown. Instead of these, Figure 5 contains curves representing the assumed "upper limit of safety" obtained by allowing the margin of safety discussed in connection with Figure 3. To these curves are added a series of normal air-injection curves obtained with the burner drilled with No. 40 ports and corresponding to several adjustments of the orifice. For the reasons given above these curves may be assumed to apply satisfactorily to the burners with ports of other sizes also. It is therefore easy to determine from a study of Figure 5 the effect upon safety from flash back and lifting of any adjustment

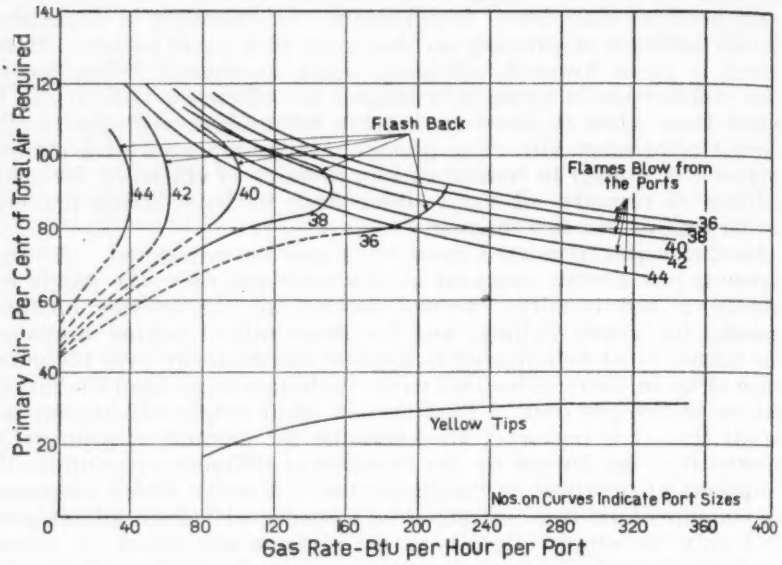

FIGURE 4.—*Effect of the size of port on the position of the flash back, lifting, and yellow-tip curves*

Port sizes, 36 to 44.

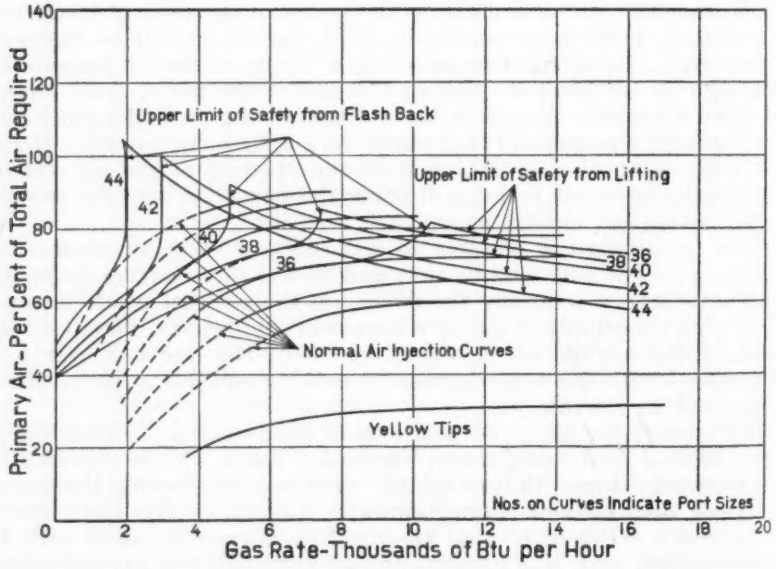

FIGURE 5.—*The assumed safe upper limit of primary air*

Port sizes, 36 to 44.

of burners of this form when drilled with ports of any size from 36 to 44. We find, for example, that a burner with No. 36 ports is safe within the prescribed limits when burning gas at 12,000 Btu. per hour and when adjusted to entrain 78 per cent of the air necessary for complete combustion. If the burner so adjusted is turned down, however, there is danger of flash back below about 10,200 Btu. per hour. Obviously, no one would want a burner on a domestic range that could not be turned lower than 10,200 Btu. per hour; hence, if No. 36 drills are to be used, a considerably lower entrainment of primary air, about 72 per cent at 12,000 Btu. per hour, is necessary. This adjustment will permit an entrainment of only 58 per cent of the air needed for complete combustion at a gas rate of 4,000 Btu. per hour. If we use No. 44 drills we can turn down the burner to

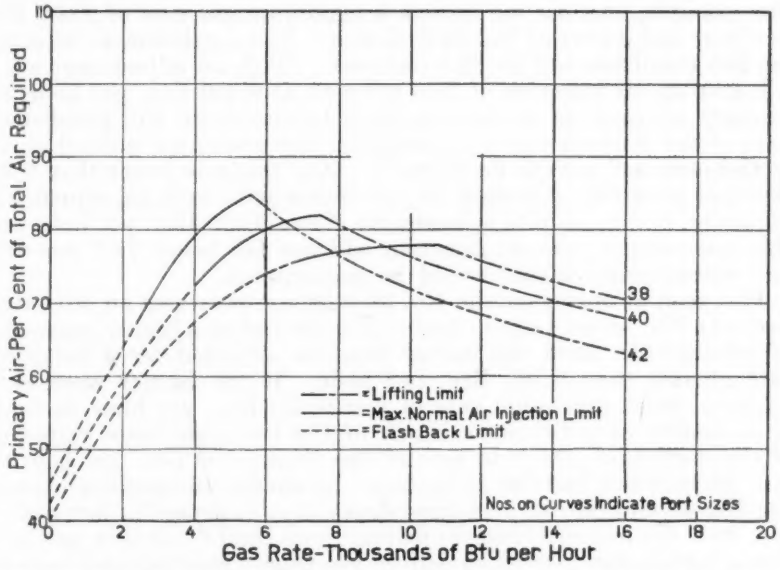

FIGURE 6.—*The upper limit of safe adjustment of primary air for each gas rate*

Port sizes, 38 to 42.

any extent without danger of flash back if we adjust it to entrain 84 per cent of the air required at 4,000 Btu. per hour; but with such an adjustment we can use only about 4,500 Btu. per hour without danger of blowing off the flames. If the burner with No. 44 ports is to be used to supply 9,000 Btu. per hour, the usual maximum rate for a standard burner, it will have to be adjusted to inject at that rate only 70 per cent of the air required.

Since the greatest difficulty in burning gas completely is encountered when the rate at which it is supplied is greatest, we are primarily concerned with the air adjustment that may be made at the maximum gas rate, and that will still be safe for all other gas rates below the maximum. Figure 6 represents, for ports drilled with Nos. 38, 40, and 42 drills, the limit of safe adjustment of primary air at each gas rate, assuming that rate to be the highest but not the lowest that will ever be used. The curves are redrawn from Figure 5 on a larger

scale to permit their easier inspection. Each limit is found, beginning at a high gas rate, such as 16,000 Btu. per hour, (1) by following the "upper limit of safety from lifting" for a given port size until it intersects the normal air-injection curve, which is tangent to the "upper limit of safety from flash back," for the same port size, (2) following this normal air-injection curve until the "upper limit of safety from flash back" is reached, and (3) following the latter curve to the zero rate

From these curves the maximum primary air for which it will be safe to make an adjustment can be obtained for any gas rate desired within the range covered. Having assumed a gas rate and determined the maximum primary-air injection, an orifice and air shutter setting which will give this injection will be safe to use at any rate lower than the assumed rate, but will not be safe at a higher rate. For example, suppose we assume a maximum gas rate of 9,000 Btu. per hour and a port of No. 40 drill size. The maximum air injection for this condition will be 78.5 per cent. With an adjustment which will give an air injection of 78.5 per cent at 9,000 Btu. per hour, the primary air injected as the burner is turned down will parallel the part of the limiting curve representing the maximum normal air injection and will always be below it. Any gas rate lower than 9,000 Btu. per hour will, therefore, be safe to use with such an adjustment. However, if the gas rate is increased above 9,000 Btu. per hour with this same orifice, the air injection will not fall below 78.5 per cent, and consequently lifting would be encountered.

It is seen at once that the No. 38 port size possesses an advantage over the No. 40 port size in permitting the use of a higher proportion of primary air when the burner must be adjusted for a maximum rate greater than 9,300 Btu. per hour. If the burner were to be adjusted for a maximum rate of just 9,300 Btu. per hour, it would be a matter of indifference which of the two sizes were employed. If the maximum rate is to be any less than 9,300 Btu. per hour the No. 40 port size has the advantage. A similar comparison between the No. 40 and No. 42 port sizes shows the advantage in favor of the No. 40 if the burner is ever to deliver more than 6,500 Btu. per hour. For a burner constructed to deliver less than 6,500 Btu. per hour the No. 42 port size would have the advantage. Considering the probable use of a range burner of the "standard" size, the No. 40 port appears to be the most favorable size to use.

With the port size determined, the total port area is also fixed, and it is now possible to determine accurately the other dimensions, such as area of mixer throat, length of mixer tube, etc., using the relations as shown in Figure 1. These dimensions may now be changed on the test burner to meet the conditions for maximum air injection if desired.[4]

3. DETERMINATION OF THE LIMIT OF COMPLETE COMBUSTION AND ITS VARIATION WITH CHANGES OF DISTANCE BETWEEN THE BURNER AND THE UTENSIL

The above determinations have been concerned with the burner alone; the remaining tests consider the appliance as a whole, especially the relation between the burner and the combustion space, which, in this case, is the distance between the burner and the utensil.

[4] In this preliminary investigation for the determination of the proper port size, the design of the mixer is of small importance, as the primary air is forced into the burner. When the burner is placed in service, however, the primary air is injected into the burner by the momentum of the gas stream, and the design should be such that the air injection is within the range desired.

The determination of whether or not combustion was complete was made by analyzing the products of combustion for carbon monoxide.[5] In this study the relationship between the amount of gas burned and the smallest quantity of primary air which would insure complete combustion was determined.

With the burner installed as before, except that in this case a utensil was placed at some known distance above it, gas was supplied at a constant rate and an amount of primary air used which gave a flame adjustment just above the yellow-tip curve. After allowing sufficient time for conditions of temperature to become constant, a sample of the products of combustion was collected and analyzed for both carbon monoxide and carbon dioxide. At the same time the percentage of

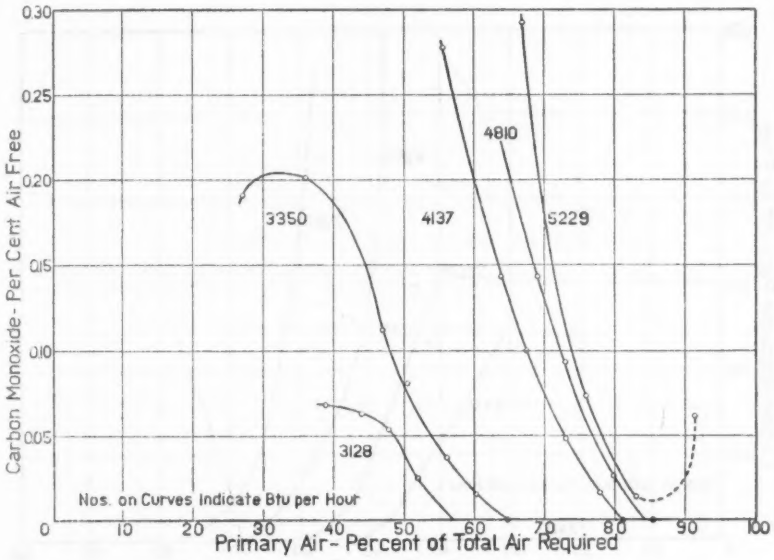

FIGURE 7.—*The effect of primary air on the production of carbon monoxide at various gas rates*

Distance between burner and utensil = ¾ inch

air in the mixture within the burner was determined. The primary air was now increased and the same procedure repeated. This procedure of increasing the primary air and analyzing the products of combustion was continued until an adjustment was made which resulted in the formation of very little, if any, carbon monoxide. Other determinations at various gas rates were made in the same manner. The percentage of carbon monoxide was reduced to an air-free basis by computation, the percentage of carbon dioxide in the sample and the theoretical percentage of carbon dioxide in the air-free products being known. This was done to correct for the amount of excess air drawn in at the time of sampling. The results were plotted as shown in Figure 7, all curves being extrapolated to the axis representing 0 per cent carbon monoxide.

[5] A description of the apparatus used for making these determinations is given in the Appendix.

It will be observed that no amount of primary air would give a zero point when a gas rate of 5,229 Btu. per hour was used because the gas rate was too great for the distance used between burner and utensil, and lifting of the flames occurred before a zero point could be obtained.[6] Figures 8 to 11, inclusive, show similar studies, each chart giving the results obtained for a different distance between burner and utensil. From these charts the amount of primary air necessary to reduce the carbon monoxide to zero for any gas rate and distance used can be readily determined. These zero points from each chart were replotted as shown in Figure 12 and labeled "0 per cent CO curves." The flash-back blowing, and yellow-tip curves obtained with the No. 40 port size and the "limit of safe adjustment" from Figure 6 were also plotted on this same chart, making it possible to

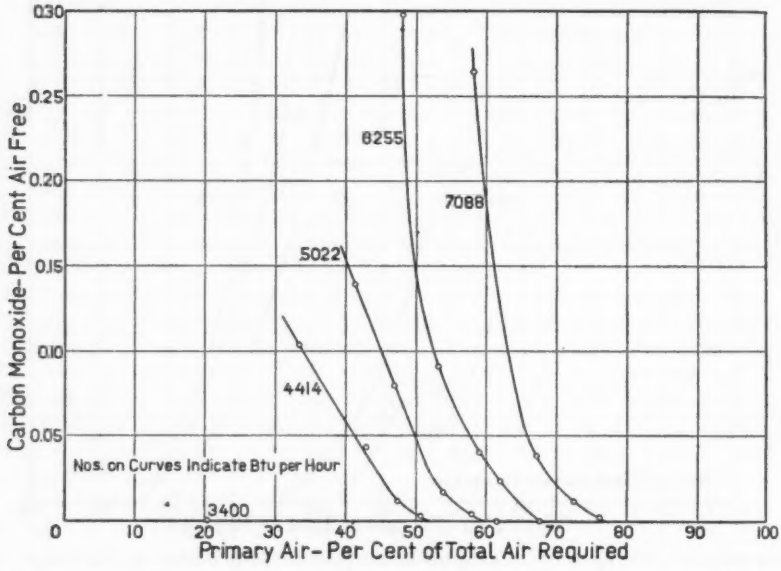

FIGURE 8.—*The effect of primary air on the production of carbon monoxide at various gas rates*

Distance between burner and utensil = 1 inch

see at a glance within what limits the burner must operate to be satisfactory at any given distance between burner and utensil. For example, suppose it was desired to use a distance of 1¼ inches, then for safe operation the burner must be adjusted for a condition which falls above the zero carbon monoxide curve for this distance, and at the same time falls below the limit of safe adjustment. It is seen immediately that the highest gas rate that can be safely used with the burner in this position is 9,200 Btu. per hour, and when adjusted for this rate 78 per cent of the air required for complete combustion must be supplied as primary air.

[6] The somewhat peculiar condition occurring in this case, which may be called "smothering," is encountered only when products of combustion partially surround the flames and exclude the normal access of secondary air. It is not to be confused with the "blow-off" which occurs at a higher rate in the presence of abundant secondary air.

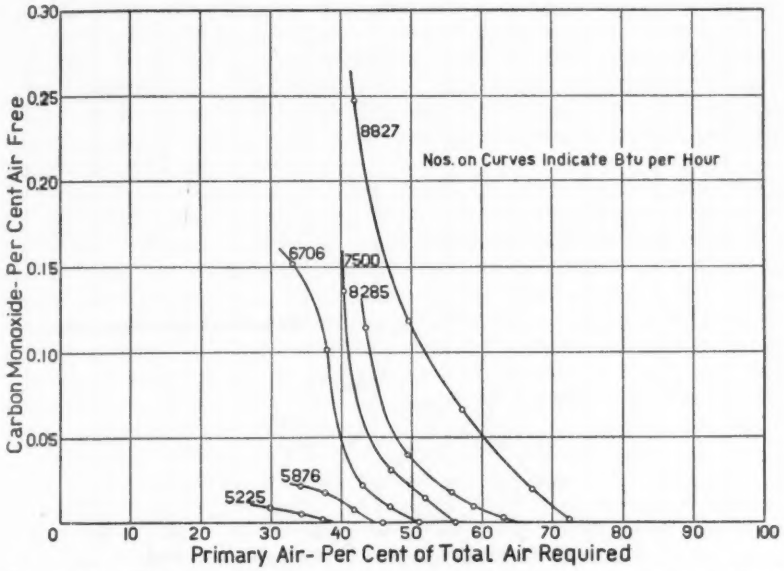

FIGURE 9.—*The effect of primary air on the production of carbon monoxide at various gas rates*

Distance between burner and utensil=1¼ inches

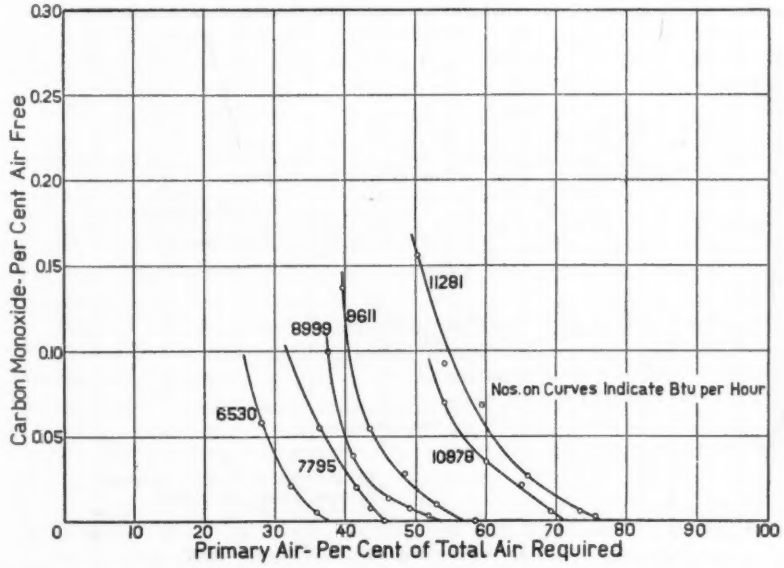

FIGURE 10.—*The effect of primary air on the production of carbon monoxide at various gas rates*

Distance between burner and utensil=1⅜ inches

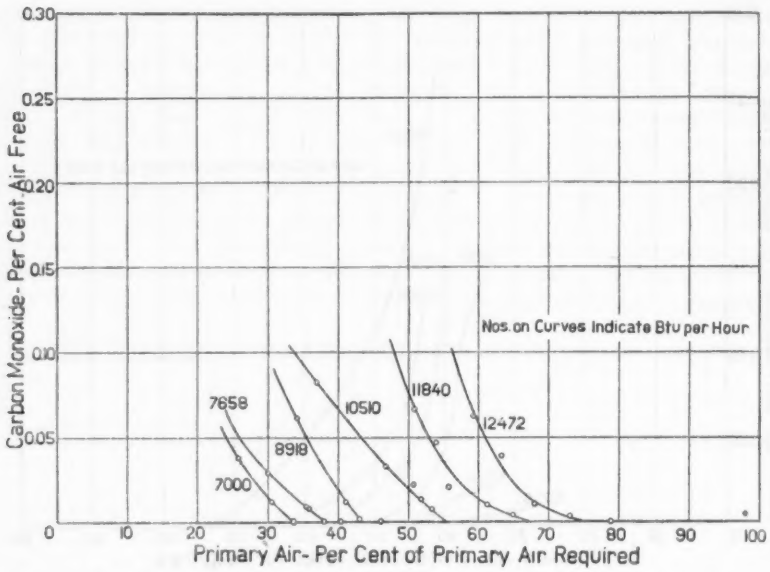

FIGURE 11.—*The effect of primary air on the production of carbon monoxide at various gas rates*

Distance between burner and utensil = 1½ inches

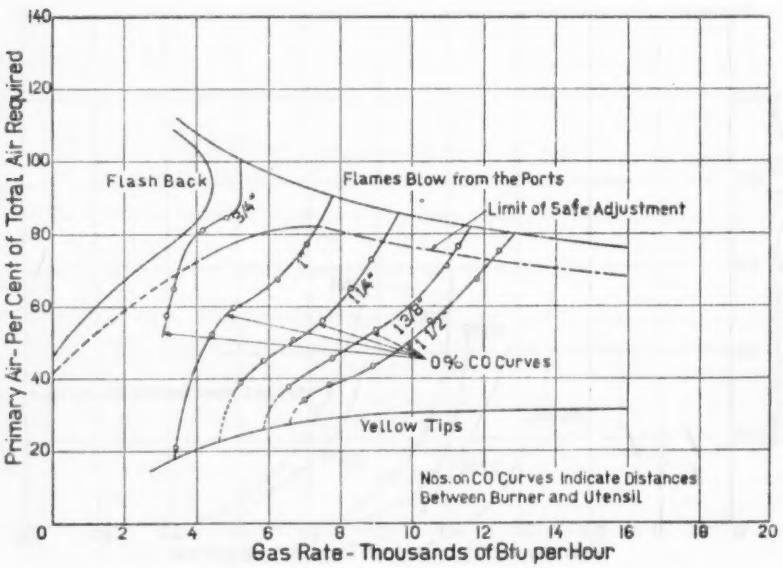

FIGURE 12.—*Combined curves showing limits of safe operation at various distances between burner and utensil*

Port size 40

It is apparent that the farther the burner under investigation is removed from the utensil, the greater becomes the area of safe adjustment, and that a distance of three-fourths inch, or less, between burner and utensil is impracticable because of the extremely limited range of operation. The highest gas rate that could be used safely at this ¾-inch distance is 3,450 Btu. per hour (the rate corresponding to the intersection between the curves representing "0 per cent CO" and the "limit of safe adjustment").

In order to show some of the information which can be gained from data such as are shown in Figure 12, several examples will be given.

1. What distance should be used between burner and utensil in order to burn gas at a rate of 9,000 Btu. per hour and with a burner capable of injecting only 55 per cent of the total air required? The intersection of the lines representing 9,000 Btu. per hour and 55 per cent primary air falls between the 0 per cent carbon monoxide curves obtained at 1¼ and 1⅜ inch distances. In order to have complete combustion it would therefore be necessary to use a distance of 1⅜ inches. A greater distance would also be safe, but would not give as high a heating efficiency. If the normal operating rate and the air adjustment are known, as is assumed in this example, then enough information is already available to select the proper distance between burner and utensil. If the burner is capable of adjustment to inject 78 per cent of the air required, however, the burner can be given this adjustment at 9,000 Btu. per hour and safely set 1¼ inches from the utensil. It will then have a higher efficiency than when placed 1⅜ inches from the utensil. It is assumed in the discussion which follows, however, that the proper gas rate is one of the unknowns; and as the distance selected not only affects the efficiency but also the maximum rate at which gas can be safely burned and the time required to accomplish a given amount of heating, a consideration of these variables is also essential before a selection of distance can be made.

2. What is the permissible range of primary air adjustment when the burner is 1¼ inches from the utensil and burning gas at a rate of 7,000 Btu. per hour? The lowest safe air injection is obtained by the intersection of the 0 per cent carbon monoxide curve for this distance and the line representing 7,000 Btu. per hour, while the highest is obtained from the intersection of the limit of safe adjustment and the 7,000 Btu. line. The permissible range is therefore from 52.5 to 82 per cent.

3. What is the maximum safe gas rate that can be used when the distance between the burner and the utensil is 1⅜ inches? The maximum safe gas rate is given by the intersection of the 0 per cent carbon monoxide curve obtained at this distance and the curve representing the limit of safe adjustment. This intersection occurs at a rate of 11,170 Btu. per hour. In order to use such a rate, however, it would be necessary to have the primary air adjusted for exactly 74.0 per cent of the total air required. A variation either way from this percentage would give an adjustment which would be either above the limit of safe adjustment or below the 0 per cent carbon monoxide curve, with either lifting of the flames or incomplete combustion as the result. A lower rate would therefore be necessary in practice, so as to allow a reasonable variation in primary air injection.

4. DETERMINATION OF RELATIVE HEATING EFFICIENCY AND ITS VARIATION WITH CHANGES OF GAS RATE, PRIMARY AIR INJECTION, AND DISTANCE BETWEEN BURNER AND UTENSIL

In addition to the factors which affect safety there are two conditions which every heating appliance must fulfill to be satisfactory to the user: (1) It must have a high heating efficiency, and (2) it must be capable of performing a given heating operation within a reasonable time.

Efficiency may be defined as the ratio of the heat transferred to the contents of the utensil to the total heat produced by the combustion of the gas. For example, the efficiency would be said to be 50 per cent if, when the gas is burned at the rate of 9,000 Btu. per hour, 4,500 Btu. is so transferred. In making a determination of efficiency, heat which goes to evaporate water from the utensil is included in that transferred. Heat which may have been transferred to the utensil, but is lost through radiation or otherwise than by causing evaporation, is not included.

The efficiency of heat transfer depends upon the size, shape, and material of the utensil and somewhat upon its temperature, which in turn depends to a certain extent upon its contents. It would be possible, therefore, to obtain a considerable variety of numerical values for efficiencies, depending upon the conditions employed during the tests. We are primarily concerned, however, with comparisons between one appliance and another rather than with absolute values. It is therefore sufficient for practical purposes to make the measurements of efficiency under a set of conditions chosen to approximate roughly the average service required of a range burner, and to reproduce carefully the same conditions in every test of a series that is to be intercompared. In the present study it was desired to determine how the efficiency is affected by variations in distance between burner and utensil, gas rate, and primary air injection. The method described below was selected because it is capable of giving the desired comparisons both accurately and with relatively few tests.

Two quarts of water (4.17 pounds) was heated to boiling. A reading of the gas meter was taken when the temperature reached 100° F. and another at 200° F. The difference between these readings (corrected to standard conditions) gave the amount of gas used in cubic feet, and this value multiplied by the heating value of the gas per cubic foot gave the Btu. delivered. The heat absorbed by the water in Btu. is the product of the number of pounds of water heated and the increase of temperature in degrees, and was the same in all tests, namely, 417 Btu. (In these tests the amount of water evaporated was negligible, and the heat required for evaporation was therefore not considered.) The efficiency was obtained by dividing the heat absorbed by the heat delivered, and multiplying the result by 100. The time required for the temperature to rise 100° F. was also recorded for each test. An aluminum utensil of light weight having a capacity of 4 quarts and a diameter of 6¾ inches at the bottom was selected for these tests as being representative of the size and material most frequently used in the average family.

For these tests the burner was installed in the same manner as that employed for the study of combustion. With the utensil set at a fixed distance above the burner, a series of determinations of efficiency was made for each of several gas rates up to the maximum safe rate

for the given distance, the primary air being varied over the entire range of safe air injections. (The maximum safe gas rate and the range of safe air injection were obtained from fig. 12.) The curves resulting when relative efficiencies are plotted against primary air, for each of four gas rates at distances of 1 inch and 1¼ inches, are shown in Figure 13. Each point on the curves represents the average of two or more determinations.

The two short vertical lines shown on each rate curve are the limits of primary air injection within which the burner must be adjusted for safety from either lifting (*L*), maximum normal air injection (*A*), flash back (*F*), carbon monoxide (*C*), or yellow tips (*Y*). For example, if a gas rate of 7,099 Btu. per hour is used with a 1-inch distance between burner and utensil, the primary air must

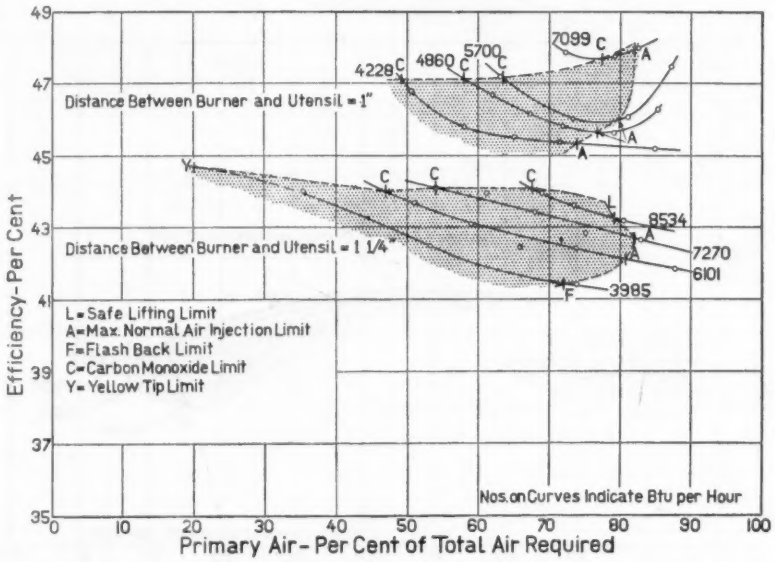

FIGURE 13.—*Variation of heating efficiency with changes in gas rate, primary air injection, and distance between burner and utensil*

Distances between burner and utensil=1 inch and 1¼ inches

be adjusted between 77 and 82 per cent. (See fig. 12.) If the air injection falls below 77 per cent, as shown by the *C* limit, then carbon monoxide will be produced, and if an adjustment is made to a higher value than 82 per cent, the flames will be in danger of flashing back when the "gas is turned down." At the highest gas rates lifting determines the upper limit of safe air injection. As the gas rate is decreased lifting is replaced by the maximum normal air injection as the upper limit of safety. This in turn is replaced by flash back at a still lower gas rate. Similarly, the gas rate used determines whether the production of carbon monoxide or the appearance of yellow tips determines the lower limit of safe air injection. By drawing a dotted line through all of the points representing the upper limits of safety and another through all of the points representing the lower limits and extending these lines until they intersect at a point

representing the maximum safe gas rate, an area is delineated within which any efficiency shown can be safely obtained.

Results obtained in a similar manner, using 1⅜ and 1½ inch distances, are shown in Figures 14 and 15, respectively.

From Figure 12 it will be noted that the maximum safe gas rate which could be used at a 1-inch distance is 7,350 Btu. per hour, and if such a rate were used the primary air injection would have to be exactly 82 per cent for safe operation. Because the highest rate used in making the efficiency tests when using the 1-inch distance was slightly below this maximum gas rate, it was necessary to ascertain the efficiency which would have been obtained at 7,350 Btu. per hour by extrapolation. This was done by selecting from the curves of Figure 13 for the 1-inch distance the efficiencies which were obtained at the required primary air adjustment of 82 per cent, for each of the

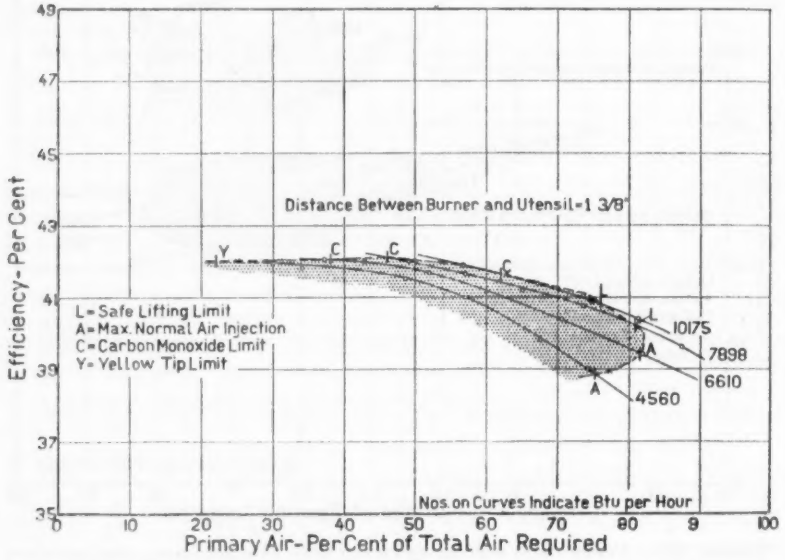
Efficiency - Per Cent
Primary Air - Per Cent of Total Air Required
Distance Between Burner and Utensil = 1 3/8"
L = Safe Lifting Limit
A = Max. Normal Air Injection
C = Carbon Monoxide Limit
Y = Yellow Tip Limit
Nos. on Curves Indicate Btu per Hour
10175
7898
6610
4560

FIGURE 14.—*Variation of heating efficiency with changes in gas rate and primary air injection*

Distance between burner and utensil=1⅜ inches.

several gas rates used. By plotting the efficiencies thus obtained against the corresponding gas rates and extrapolating this curve to the maximum safe gas rate, the efficiency which would have been obtained had such a rate been used was ascertained. Figure 16 shows the curves plotted in this manner for each of the four distances used, the maximum safe gas rate, and the required primary air adjustment being obtained in each case from Figure 12.

It is realized that some error is introduced in such an extrapolation and that high accuracy would require an actual determination at this maximum adjustment. Such a setting, however, is extremely difficult to make and the additional accuracy attained would not be worth the time required. If the highest rate used in the tests is reasonably close to the maximum safe rate, the error caused by such an extrapolation is small.

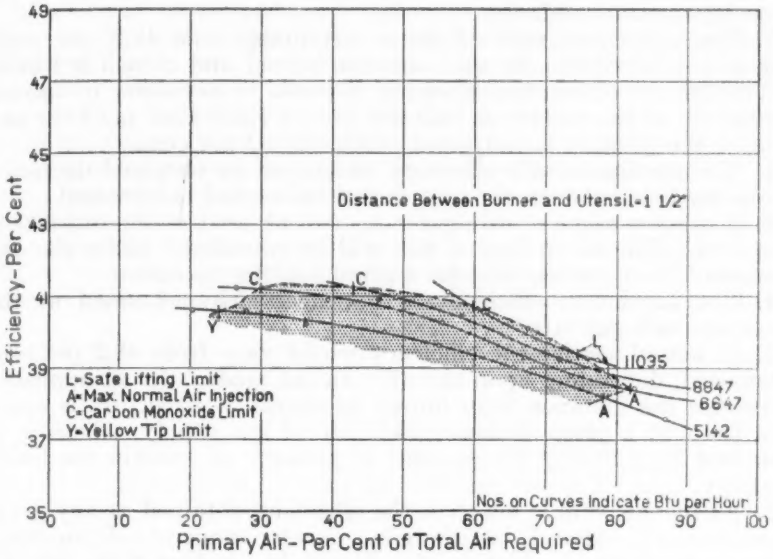

FIGURE 15.—*Variation of heating efficiency with changes in gas rate and primary air injection*

Distance between burner and utensil=1½ inches.

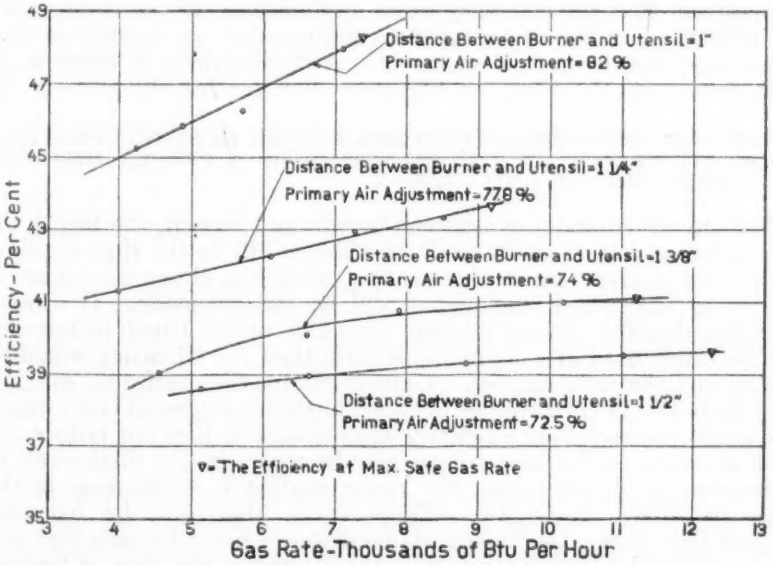
Efficiency-Per Cent
Distance Between Burner and Utensil=1"
Primary Air Adjustment=82 %
Distance Between Burner and Utensil=1 1/4"
Primary Air Adjustment=77.8 %
Distance Between Burner and Utensil=1 3/8"
Primary Air Adjustment=74 %
Distance Between Burner and Utensil=1 1/2"
Primary Air Adjustment=72.5 %
▽=The Efficiency at Max. Safe Gas Rate
Gas Rate-Thousands of Btu Per Hour

FIGURE 16.—*Efficiencies obtained at the various gas rates used and with the primary air adjustment required at the maximum safe gas rate for each distance between burner and utensil*

A summary of the information which can be obtained from Figures 13 to 16, inclusive, follows:

1. The maximum safe efficiency attainable was 48.2 per cent. This is possible if the distance between burner and utensil is 1 inch, and in order to obtain this efficiency it would be necessary to operate the burner at the maximum safe gas rate of 7,350 Btu. per hour and to have the primary air adjusted at exactly 82 per cent.

2. The maximum safe efficiency which can be obtained decreases as the distance between the burner and the utensil is increased.

3. A greater range of safe gas rates can be used as the distance is increased. The advantage of this will be considered under the discussion of the time required for a given heating operation.

4. The maximum efficiency is not necessarily obtained at the maximum safe gas rate.

5. In actual service the efficiency would vary from 48.2 per cent downward, depending upon the adjustment made. In an appliance in service the distance from burner to utensil is fixed. It is easily seen that, at a given distance and rate of gas supply, efficiency is increased by reducing the amount of primary air, within the limits of safety.

6. As the gas rate is lowered, the efficiency obtained at any given air injection is reduced, but there is a greater range of safe air injection, as is shown in Figure 12. Stated in another way, for any setting of the air shutter in service (at a given setting the proportion of primary air is nearly constant), the efficiency is increased by increasing the rate at which gas is burned, within the limits of safety.

The effects on efficiency of changing the adjustments of appliances in service are thus clearly shown. It is evident that the common supposition that the efficiency of an appliance in service is decreased by adjusting, or by changing the conditions of gas supply so that more heat is delivered, is incorrect. A similar error is often made with respect to the effect on efficiency of increasing the primary air.

5. THE TIME REQUIRED TO PERFORM A GIVEN HEATING OPERATION AND ITS EFFECT ON THE SELECTION OF A PROPER DISTANCE BETWEEN BURNER AND UTENSIL

For any given distance between burner and utensil, the higher the gas rate that can be safely used the shorter will be the time required to perform a given amount of heating, while the closer the burner is placed to the utensil the higher will be the efficiency. If it were possible, therefore, to use as high a gas rate at the 1-inch distance as can be safely used at a 1½-inch distance, then the efficiency would be higher and the time shorter. Unfortunately, the maximum safe gas rate decreases as the distance between burner and utensil is decreased and since the increased efficiency thus obtained does not reduce the time as much as the lowered gas rate increases it, the final result of a decrease in distance over the range studied is an increase in the time required. These two effects must, therefore, be balanced against each other, the most suitable distance being the one that will produce the highest efficiency without increasing the time of heating beyond a certain predetermined value.

The selection of such a time limit is arbitrary and must be decided by the designer from the requirements of his particular problem.

The relation between efficiency and time is shown in Figure 17. As previously mentioned, the maximum efficiency does not always occur at the maximum safe gas rate. Therefore, the maximum efficiency which can be obtained at any given distance does not necessarily correspond with the adjustment which would allow the transfer of a given amount of heat in minimum time. The only condition under which these two factors do correspond is that in which the maximum efficiency is obtained at the maximum safe gas rate. Accordingly, two efficiency curves are shown, one obtained by selecting as points the maximum safe efficiency at each distance and the other by plotting the efficiency obtained at the maximum safe gas rate for each distance, which is also the efficiency at minimum time. In the present study the 1-inch distance is the only one at

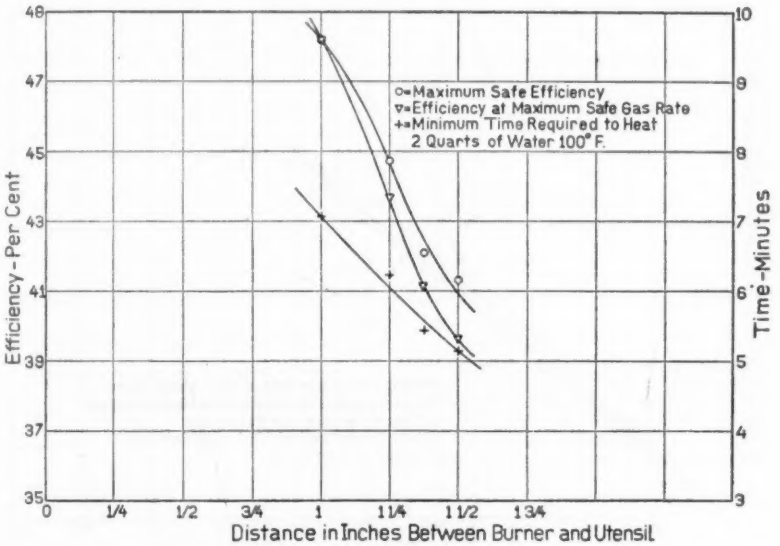

FIGURE 17.—*The maximum safe efficiency and the efficiency at the maximum safe gas rate for each of the distances used. The minimum time required to heat 2 quarts of water 100° F. at each of the distances used.*

which these points exactly correspond. The time curve shown corresponds to the efficiency curve obtained from the maximum safe gas rate, which will, therefore, be the minimum time required. It is evident from this curve that the minimum time required to heat 2 quarts of water 100° F. increases from 5.2 to 7.1 minutes (37.3 per cent) as the distance is decreased from 1½ inches to 1 inch. It is also apparent that a sacrifice of efficiency must be made if this increase in time is to be prevented.

Another method of representing these relations is shown in Figure 18, where the gas rate in Btu. per hour is plotted against the heat absorbed in Btu. per hour. The heat absorbed is the product of the heat delivered in Btu. per hour by the efficiency. The point on each curve marked by a triangle is the maximum safe gas rate that can be used at the distance indicated.

If we assume that we are able to adjust the gas pressure and hold it constant by means of a regulator or some other suitable device, it is now possible to select the best distance between burner and utensil, and also the proper gas rate to give the highest safe efficiency consistent with a reasonable time of heating.

In terms of heat absorbed per hour, any rate above 2,700 Btu. will be considered as satisfactory.[7] Figure 18 shows that it is possible with the burner used to obtain much more rapid heating than this at any of the distances shown.

It is necessary to consider efficiencies as well as speed. In Figure 19 the maximum safe efficiency at each gas rate represented in the efficiency diagrams (figs. 13 to 15) is plotted against the corresponding rate of heat absorption. The solid lines are drawn to represent the

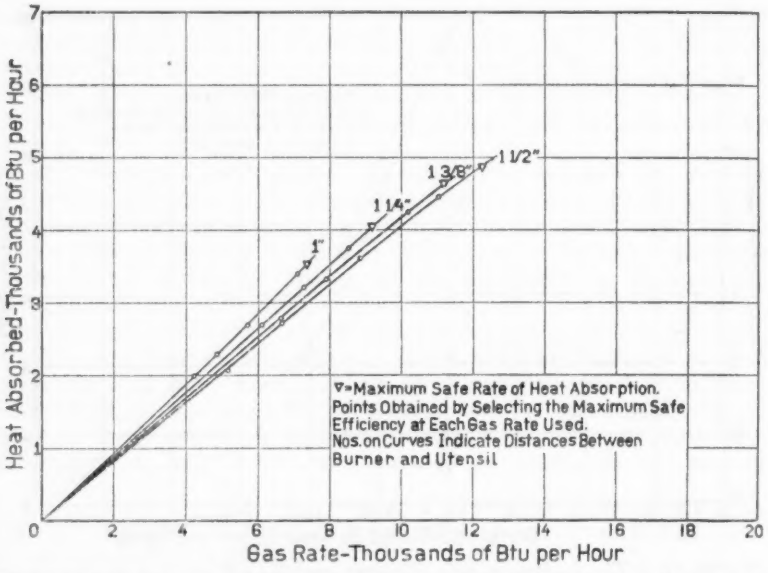

FIGURE 18.—*Rate of heat absorption corresponding to the maximum safe efficiency at each gas rate used.*

trend of these results. It will be observed that within the range of experiment the best efficiency obtainable at each distance between burner and utensil is nearly independent of the rate of heating, but tends at first to increase as the rate of heating is reduced, especially for the greater distances between burner and utensil. It must eventually fall to zero (at the rate required to maintain a temperature of 200° F. in the utensil used in the efficiency test), but the lower parts of the curves have not been determined. If the appliance is adjusted for maximum efficiency at the maximum safe rate for heat transfer and subsequently turned down, as it would be in practice, without a readjustment of the air supply, the efficiencies follow the trend indicated by the crosses and the dotted lines. These data were obtained as follows: The maximum gas rate and the primary air required for

[7] This limit is based on the "approval requirements" of the American Gas Association for gas ranges, which grants approval to appliances with standard burners which have an "input rating" of 9,000 Btu. per hour and an efficiency of 30 per cent.

safe combustion were obtained from Figure 12. The corresponding point was located by following to the left the nearly horizontal curves in Figure 20, which represent the amount of primary air injected; the primary air at each rate as the burner is turned down was easily located. (The method by which the curves of fig. 20 were obtained is discussed in section 6.) Reference was then made to Figures 13 to 15 to determine the efficiency at the rates for gas and primary air in question. This efficiency was multiplied by the gas rate to determine the rate of heat transfer and the result plotted in Figure 19. Probably the most interesting result which appears from this figure is that under all conditions the efficiency decreases as the gas is turned down without changing the adjustment of air. Stated in another

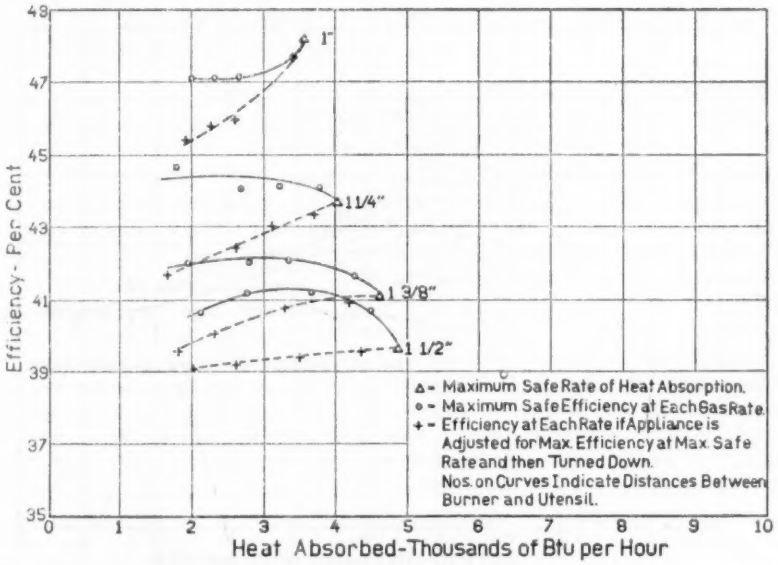
Efficiency - Per Cent
Heat Absorbed-Thousands of Btu per Hour
1"
1 1/4"
1 3/8"
1 1/2"
△ - Maximum Safe Rate of Heat Absorption.
○ - Maximum Safe Efficiency at Each Gas Rate.
+ - Efficiency at Each Rate if Appliance is Adjusted for Max. Efficiency at Max. Safe Rate and then Turned Down.
Nos. on Curves Indicate Distances Between Burner and Utensil.

FIGURE 19.—*Relation between efficiency and rate of heat absorption at each distance used*

way, efficiency increases as the rate of heating is increased until the limit of safety is passed.

From Figures 18 and 19 it is apparent that the efficiency which can be obtained decreases but that the possible rate of heating increases as the distance between burner and utensil is increased. If speed were the only consideration, then the distance selected would be 1½ inches, but from the standpoint of economy it would be better to use a 1-inch distance, because the highest efficiency can be obtained at this distance and a satisfactory rate of heating as well.

With the pressure fixed it would be safe at this distance to use a gas rate of 7,350 Btu. per hour, which will allow a rate of heat absorption of 3,540 Btu. per hour and give a heating efficiency of 48.2 per cent.

The air injection required at a gas rate of 7,350 Btu. per hour at the 1-inch distance was previously determined from Figure 12 to be 82 per cent; it is now necessary to determine the size of orifice which will give this air injection.

6. NORMAL AIR INJECTION AND ITS VARIATION WITH ORIFICE SIZE

In all of the previous tests the orifice size was unimportant because the primary air was forced into the burner. It was merely necessary to use a size which would allow the gas to pass at the desired rate under the range of pressure available. However, when an appliance is installed for use, the primary air is drawn into the burner by the energy of the gas stream issuing from the orifice, and the amount thus injected depends in part upon the size of the orifice. When using any given rate of gas supply the amount of air injected increases as the size of the orifice is decreased.

For the determination of this relation the burner was connected to a source of gas supply only, the air mixer being left open to the air of

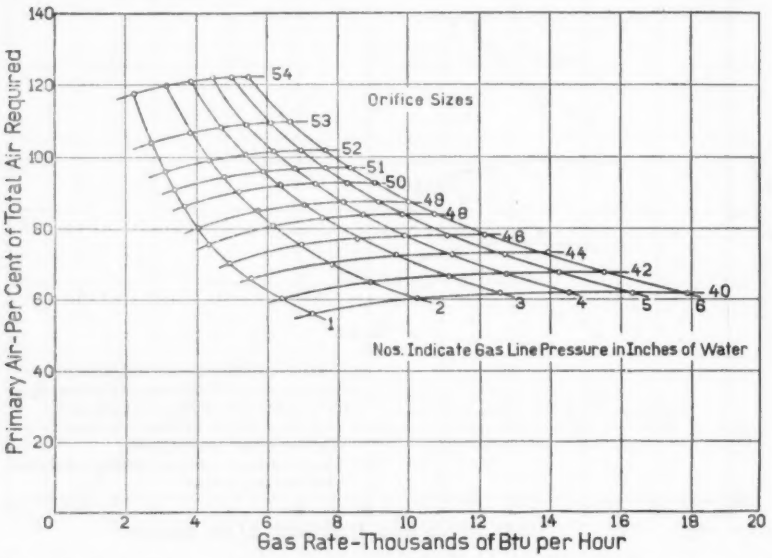

FIGURE 20.—*The primary air injected by gas at different rates with various pressures and orifice sizes*

the room. The burner used was provided with an air shutter, and this was set in its wide-open position. With an orifice of known size,[8] the burner was then operated at a number of different gas pressures and the ratio of air to gas within the burner head and the gas rate were determined for each setting. The same procedure was repeated with orifices of as many different sizes as was desired. The results have been plotted in Figure 20, from which it is possible to select not only the proper orifice size to give the desired air injection, but also the gas pressure needed to give the desired gas rate.

From these curves it is apparent, for example, that the largest orifice which will give an air injection of 82 per cent when passing gas at a rate of 7,350 Btu. per hour is a No. 48, and the pressure necessary to

[8] The results shown in Figure 20 were obtained by the use of a number of fixed orifices of different sizes. It is customary for most range manufacturers to supply the range with adjustable orifices. Such an orifice could be studied in the same manner as described above by making determinations at a number of different settings of the same orifice.

deliver the gas at the required rate with this orifice is approximately 2⅞ inches of water. If the pressure is below 2⅞ inches, satisfactory entrainment of air is impossible with this burner at the 1-inch distance from the utensil, when using the desired gas rate, because carbon monoxide will be produced if the air injection is below 82 per cent. At a higher pressure a smaller orifice must be used to deliver gas at the desired rate, and the air shutter must be partially closed to control the amount of primary air, because lifting occurs above 82 per cent.

III. EFFECTS OF VARIATIONS IN GAS PRESSURE AND OF UNCERTAINTIES IN THE ADJUSTMENT OF BOTH GAS RATE AND PRIMARY AIR ON THE SAFE RANGE OF PRIMARY AIR ADJUSTMENT, THE SAFE DISTANCE BETWEEN BURNER AND UTENSIL, AND THE HEATING EFFICIENCY OBTAINABLE

It is obvious from the last paragraph that the appliance can not safely be constructed and adjusted to employ the optimum conditions unless both the pressure and the adjustment of primary air are subject to accurate control. The gas pressure in any given locality is usually variable, and unless some means for controlling this variation is available it is necessary to adjust a burner so that safe conditions will prevail over the range of pressures which will actually be encountered.

In order to allow for such fluctuations of pressure, the American Gas Association requires that the appliance be capable of meeting all of the requirements for safety when it is adjusted to deliver gas at the "normal" rate at one pressure and is then subjected to pressures 50 per cent above and below that for which the adjustment was made. Not only is it necessary to take practical account of the variations of pressure to which an appliance will be subjected, but it is also necessary to consider the uncertainty whether the primary air will be adjusted with the required accuracy. The problem of making suitable allowances for the effect of these variations which will be encountered in service can probably be most readily understood by considering an example.

Let us assume that the appliance has been adjusted to a gas rate which will permit the transfer of heat to the utensil at the "normal" rate of 2,700 Btu. per hour at the "normal" pressure of 3.5 inches. An inspection of Figure 19 shows that if the burner is placed 1 inch from the utensil an efficiency of 47.2 per cent will be obtainable. $2{,}700 \times \frac{100}{47.2} = 5{,}710$ Btu. per hour will therefore have to be supplied. Referring back to Figure 13 we find that with this gas rate the maximum efficiency of 47.2 per cent is obtainable only when the primary air is reduced to 63.5 per cent, the limit of safety for gas burned at 5,710 Btu. per hour. With this rate the safe range of primary air lies between 63.5 and 80.0 per cent. If the pressure is to be increased 50 per cent, from 3.5 to 5.25 inches, without readjusting the appliance, gas will be delivered at the rate of $5{,}710 \sqrt{1.5} = 7{,}000$ Btu. per hour, and the adjustment of primary air must be such as to permit the satisfactory combustion of gas at this higher rate. Referring now to Figure 12, we find that at least 76 per cent of the air required must be introduced as primary air if gas is to be burned safely at 7,000 Btu. per hour. If the burner is adjusted so that 76 per cent of the air required is injected at a

gas rate of 7,000 Btu. per hour, then at a gas rate of 5,710 Btu. per hour the appliance would inject 73 per cent of that required (this number is obtained by interpolating in fig. 5) instead of the 63.5 per cent required to permit an efficiency of 47.2 per cent. This in turn reduces the available efficiency to 46.1 per cent at a gas rate of 5,710 Btu. per hour. (Fig. 13.) This lower efficiency corresponds to a rate of heat absorption of only 2,630 Btu. per hour. If 2,700 Btu. per hour is desired, the rate at which gas is supplied must be increased by a small amount. This process of trial and error can be continued until corresponding efficiencies, rates, and air adjustments have been determined with an accuracy as great as the experimental data justify. By such a series of approximations it is found that the appliance must be adjusted to take at least 5,860 Btu. per hour at the normal pressure of 3.5 inches with an efficiency of 46.1 per cent if heat is to be transferred to the utensil at the rate of 2,700 Btu. per hour and the operation of the appliance is to be safe without readjusting when the pressure is increased 50 per cent. After increasing the pressure 50 per cent the gas rate will be 7,180 Btu. per hour and the permissible air adjustment 79 to 82 per cent. (See fig. 12, 1-inch distance.) To keep within these limits of primary air at the higher pressure, the appliance will have to be adjusted at normal pressure to take primary air between the limits of 77 and 80 per cent of the total air required.

There is very little chance that in practice the adjustment of primary air will be made within this degree of accuracy. Appliance adjusters usually regulate primary air by their judgment of how the flame should appear, and there is not much difference in the appearance of the flame when primary air varies from 60 to 80 per cent of that required for complete combustion. It is therefore necessary to provide unusual means to insure correct adjustment in service, or to make the distance greater and so sacrifice the efficiency obtainable when the utensil is placed close to the burner.

By a series of approximations like that used for the 1-inch distance between burner and utensil the permissible range of air adjustments (shown by the distance between the curves representing the upper and the lower safe limits for primary air) may be found for each of the other distances for which data are available, and for other ratios of maximum pressure to pressure at the time of normal adjustment. The data obtained are plotted as solid lines in Figure 21. This figure enables one to see at a glance the effect of any variation in pressure conditions on the permissible air adjustment.

Referring to the example discussed above in which the maximum pressure was assumed to be 1.5 times the pressure at normal adjustment, the permissible variations in primary air corresponding to this condition, at the various distances used, are shown by the solid curve marked "1.5." From the same figure it is easy to determine what will be the effect of any inaccuracy in the adjustment of either the gas rate or the air injection by the appliance adjuster. If the gas rate is likely to be set higher than intended by the designer, the effect may be allowed for by considering the pressure required to produce the excess as an increment to be added to the maximum pressure and correspondingly increasing the ratio of the maximum pressure to that at normal adjustment. We may make allowance for the error anticipated in the adjustment of primary air by drawing curves parallel to and within the limiting curves of Figure 21, at

distances from them corresponding to the assumed uncertainty in this operation. As an example, it will be assumed that the maximum pressure will not exceed the pressure at the time of adjustment by more than 50 per cent. If there is no error in adjustment, the limit of safe adjustment would be within the solid curve marked "1.5" in Figure 21. Dotted lines are drawn showing the limits within which the workman should attempt to adjust the primary air if he is likely to make an error of 10 per cent of the total air required for complete combustion in either direction from the adjustment attempted. Thus, if the burner is set 1¼ inches from the utensil, the air must be adjusted between 53 and 80 per cent for safety. The dotted curve represents the assumption that the adjuster will always stay within these limits if he tries to adjust between 63 and 70 per cent.

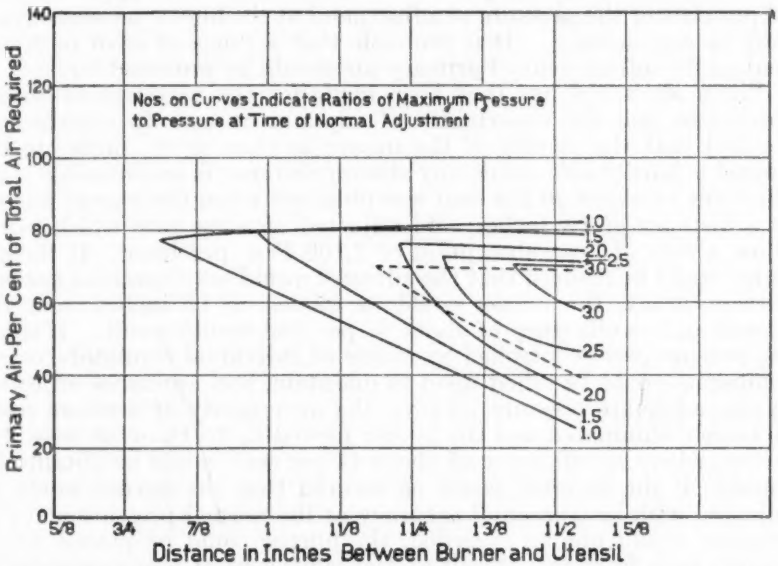

FIGURE 21.—*Effect of variations in gas pressure and uncertainties in the adjustment of both gas rate and primary air on the safe range of primary air adjustment and the safe distance between burner and utensil*

Probably the most common practice in the adjustment of appliances is for the adjuster merely to set what appears to his practiced eye to be a "good flame," with respect to the quantities of both gas and primary air. The adjustment is made without measurements of any kind; and much worse than this, it is usually made to give the desired result at the pressure which exists when the adjustment is made, without accurate knowledge or consideration of changes of pressure which will take place subsequently. In some cases adjusters are required to make an accurate adjustment of the gas supply to the manufacturer's rating by timing the meter; but this precaution is of little use when the adjuster is working, for example, in the middle of a July afternoon and has no idea whether the pressure on a January morning in that locality is likely to be greater or less than that observed.

In most cases a gas company endeavors to maintain a pressure which will not vary at any one place by more than 100 per cent of the minimum. Although in many cases it does not succeed in this, the extremes of pressure (both high and low, depending on the distance from the source of supply) usually come during the periods of the morning and evening cooking load. If these periods are avoided when making adjustments, as will usually be the case, it is reasonably safe to assume that the pressure to which the appliance will be subjected after adjustment will not be more than double that at the time of adjustment (R is not greater than 2). If the adjusters are not instructed to determine the gas rate accurately by means of the meter, a probable error in the estimated rate of at least 10 per cent should be allowed for. This corresponds to about 20 per cent difference in pressure at the pressure of adjustment and approximately 43 per cent of the pressure of adjustment at the higher pressure which may be encountered. It is probable that a range of error of 20 per cent in the adjustment of primary air should be provided for.

When allowance has thus been made for the variation of service conditions and the uncertainty of adjustment usually encountered we find that the placing of the burner as close as 1½ inches to the utensil is hardly safe, while any shorter distance is inadmissible. An efficiency of about 40 per cent was obtained when the burner was set at a distance of 1½ inches, and adjusted at a gas rate which would allow a rate of heat absorption of 2,700 Btu. per hour. If the designer could be assured that the adjuster would set a specified gas rate with accuracy, the burner could be moved to 1⅜ inches from the utensil and an efficiency of about 41 per cent would result. If either the pressure were controlled by means of individual regulators, or gas companies could be relied upon to maintain, and appliance adjusters to use, adequate pressure surveys, the uncertainty of pressure could be largely eliminated and the burner moved up to 1⅛ or at most 1$\frac{1}{16}$ inches, where an efficiency of about 44 per cent would be obtainable. Finally, if the designer could be assured that the burner would be adjusted with instrumental accuracy at the normal pressure and this pressure would not be exceeded, the burner could be placed seven-eighths inch from the utensil and an efficiency of approximately 50 per cent (obtained by extrapolation) would be practicable.

IV. ACKNOWLEDGMENTS

The method of experimental study described in this paper has been developed gradually during the varied work of several years. During this time the authors have been ably assisted in collecting data by the following men: John Corsiglia, R. W. Heywood, Oscar Tow, G. H. Cash, Otto Lutherer, N. L. Miller, B. D. Jenkins, and C. J. Merritt, all research associates from the American Gas Association Testing Laboratory; and S. A. Guerrieri, S. L. Earle, C. Creitz, W. Criswell, J. H. Branham, and H. W. Bailey, of this bureau.

V. APPENDIX

1. AN OUTLINE OF THE IODINE PENTOXIDE METHOD FOR DETERMINING SMALL QUANTITIES OF CARBON MONOXIDE IN THE PRODUCTS OF COMBUSTION

The determination of the amount of carbon monoxide present in the products of combustion is important as a criterion of the completeness of combustion and of the safe operation of gas appliances. The apparatus here described is a modification of one designed and used by the Chemical Warfare Service during the war. This method is based on the reaction of carbon monoxide (CO) and iodine pentoxide (I_2O_5) which results in the liberation of iodine and the formation of carbon dioxide according to the equation $I_2O_5 + 5CO = I_2 + 5CO_2$. The liberated iodine is absorbed in potassium iodide (10 per cent solution) and the amount determined by titration with a standardized solution of sodium thiosulphate ($Na_2S_2O_3.5H_2O$). Since the amount of liberated iodine and the volume of sample passed through the apparatus are known, the amount of carbon monoxide in the products of combustion (as sampled) can be calculated. Because the samples usually contain various amounts of excess air, it is necessary to compute the results to an air-free basis in order to compare various tests. The amount of excess air may be computed by determining free oxygen; but it is usually more convenient in routine work to determine the amount of carbon dioxide and the total volume of products, including nitrogen, formed by the combustion of a unit volume of gas, and to subsequently determine only carbon monoxide and carbon dioxide in the samples taken.

Figure 22 shows the details of construction of the iodine pentoxide apparatus designed at the Bureau of Standards. *A* is a nichrome wound resistance furnace heating a porcelain tube of about 7 mm inside diameter filled with palladium asbestos. The furnace should heat this tube to a temperature of about 700° to 750° C. *B* is a mercury sealed trap containing just enough mercury to cover the tip of the tube *C*. *D* is a float valve. The hollow, ground glass ball *E* must rise in water and seat with certainty. *F* is a specially made wash bottle of the Greiner-Friedrichs type. It is filled with concentrated sulphuric acid approximately saturated with potassium bichromate at room temperature. The liquid is introduced through the funnel marked "*G*," which connects with the bottom of the wash bottle, as does also the tube *H* through which the wash bottle is emptied. The V-shaped tube, *I*, is filled with phosphorus pentoxide and so designed that it can be easily filled or emptied without removal from the train. *J* is a tube containing iodine pentoxide supported on glass wool. *K* is a Gomberg absorption bulb, and *L* is a second mercury trap similar to *B*. *M* is an air bath insulated with approximately one-half inch of silocel, for the immersion of the absorber *F*. It is heated by means of an electric heating coil wound around the interior of the container, and capable of heating the air to a temperature of 100° C. *N* is another insulated air bath heated to a temperature of about 150° C. The temperature of both of these air baths can be controlled by means of variable external resistances.

Briefly, the operation of the iodine pentoxide apparatus is as follows: The sample is drawn into the train at *D* by means of suction applied

at the outlet of mercury trap *L*. The water used to displace the sample from the sampling tube ultimately acts upon the float *E*, causing it to rise to its upper seat. This automatically cuts off the flow through *D*. As long as the sample is flowing in at *D* the mercury in the trap *B* is sufficient to keep air from entering at *A*, but as soon as the float closes this mercury seal is broken and air for purging

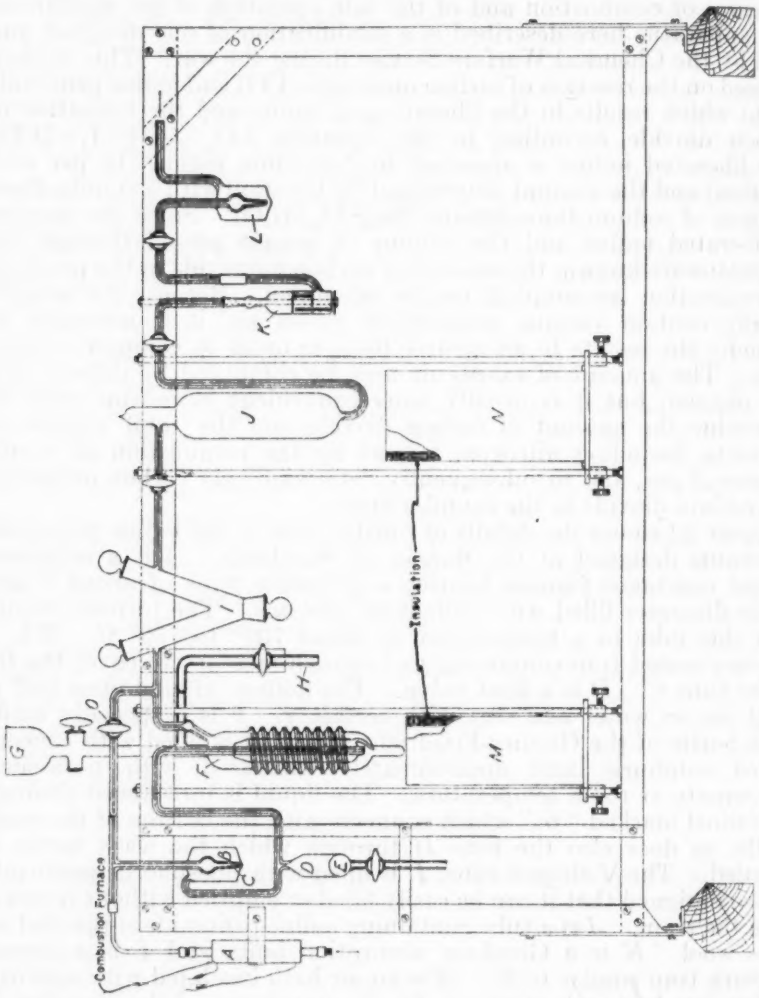

FIGURE 22.—*Iodine pentoxide apparatus for the determination of small quantities of carbon monoxide*

the train enters through the electric furnace, where any traces of carbon monoxide which might be present are burned to carbon dioxide. If the room air is free from carbon monoxide, or if air from outside can be used, this furnace can be dispensed with. It is also possible to purge the train with some inert gas, such as nitrogen, which can be supplied from a cylinder. From *D* the sample passes through wash bottle *F*, where the hot chromic acid oxidizes any materials other than carbon monoxide which are likely to be present

and which will reduce iodine pentoxide. Sulphur dioxide, hydrogen sulphide, ethylene, and some other substances are quantitatively removed by such a solution at 100° C. Carbon monoxide is not affected. This absorber also serves to remove all but a little of the water vapor. From *F* the sample passes into *I*, where the phosphorus pentoxide removes the remaining water vapor, as well as any acid spray which might have come over from *F*. In *J* the carbon monoxide reacts with the iodine pentoxide, as stated in the equation above; the iodine and carbon dioxide which are liberated pass into the Gomberg bulb *K*, where the iodine is absorbed by the potassium iodide solution. After the sample has been passed through the apparatus the train is purged with air long enough to insure that all of the sample has passed into *J* and the iodine liberated all swept into the absorption bulb. The stopcock at the outlet of *K* is closed and the pressure in the system brought to atmospheric by opening the by-pass cock *O*. The Gomberg bulb is then removed, its contents transferred to a flask and titrated with sodium thiosulphate, using starch as an indicator.

It is necessary to make sure that no iodine is being liberated before the sample is introduced into the train. This is done by purging with air for the same length of time as is necessary for the analysis of the sample, and then adding a few drops of the indicator to the contents of the Gomberg bulb. If no blue color appears the apparatus is ready for use.

This method is suitable for analyzing samples containing less than 1 per cent of carbon monoxide. The method comprises a direct determination of the amount of carbon monoxide, and it is therefore used to calibrate other types of apparatus used for carbon monoxide determinations. Its chief disadvantages are the time required for making a determination (about one half-hour) and the continual care necessary to keep the apparatus in running order. It is sensitive to amounts of carbon monoxide as small as 0.001 per cent, and its precision is about 0.003 per cent by volume. The usual sample for small amounts of carbon monoxide is 500 ml.

2. APPLICATION OF THE THERMAL-CONDUCTIVITY METHOD OF GAS ANALYSIS TO THE STUDY OF GAS APPLIANCES[1]

The analysis of gases by the "thermal-conductivity method" is based on the following principle: Assume a wire to be surrounded by a gas which is contained in a chamber the walls of which are maintained at a constant temperature. When a source of constant electromotive force is applied to the wire its temperature rises above that of the walls until a steady state is reached in which the rate of heat transfer from the wire to the walls is equal to the rate at which heat is generated by the current in the wire. The energy is dissipated by radiation, by conduction through the connections to the ends of the wire, by currents of gas circulating in the atmosphere surrounding the wire, and by conduction through the gas. Some heat is also carried away by the current of gas in case there is a flow of gas past the wire.

By a proper arrangement of conditions, all heat losses except by conduction through the gas surrounding the wire can be reduced

[1] A general discussion of the thermal-conductivity method of gas analysis is given by Palmer and Weaver in B. S. Tech. Paper No. 249.

to a minimum. The most important loss, that by convection, is largely eliminated by making the inside diameter of the cell about 1 cm. Under such conditions, it is evident that the equilibrium temperature attained by the wire will depend mainly upon the ability of the gas which surrounds the wire to conduct heat, this temperature being lower when the gas has a high conductivity, and higher

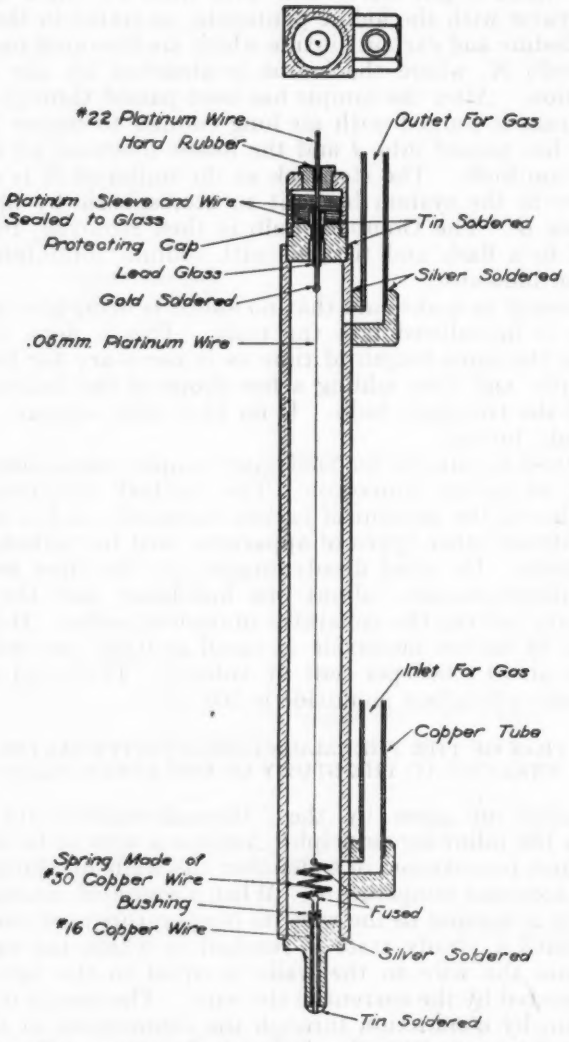

FIGURE 23.—*Section of thermal conductivity unit*

when the gas has a low conductivity. If the wire used has a high temperature coefficient of electrical resistance, the resistance will vary measurably with the thermal conductivity, and therefore with the composition of the surrounding gas. By the comparison of the resistances of two such wires mounted in suitable cells and surrounded respectively, by a reference gas and a mixture of two gases of which

the qualitative composition is known, the quantitative composition of the mixture can be rapidly and accurately determined after an empirical calibration has been made. Figure 23 is a longitudinal section through a cell showing the details of construction.

As a convenient method for comparing the resistances of the two wires, a shunted slide wire provided with extension coils is connected in parallel with the two wires of the thermal conductivity cells to form a balanced Wheatstone bridge. The apparatus employed is represented diagrammatically in Figure 24. By choosing suitable shunts and end coils, the instrument may be made to have the range and sensitivity most favorable for the measurements to be made. One terminal of a galvanometer is joined to the common connection between the two cells, and the other terminal is connected to the contact of variable position on the slide wire.

If accurate measurements are to be made, the walls of the cells must be maintained at a constant temperature. This may be done

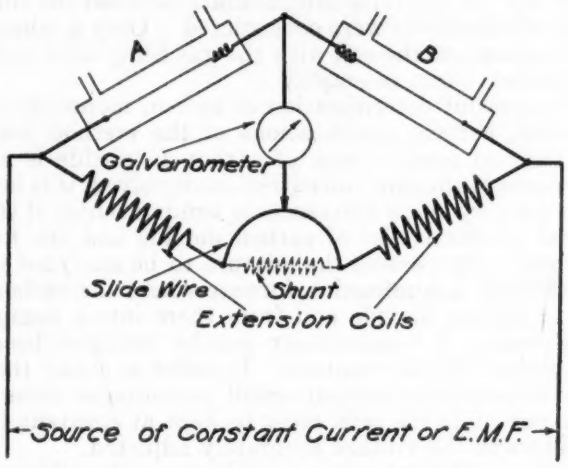

FIGURE 24.—*Wiring diagram of the air-gas ratio apparatus*

by immersing them in an oil bath, kept at constant temperature, or by clamping them in a metal block which is kept at constant temperature by means of a bimetallic strip thermostat.

The applications of the method of interest in connection with this paper are the determination of the relative proportions of gas and air in burners and the determination of carbon monoxide and carbon dioxide in products of combustion from gas appliances.

The first of these applications is extremely simple and consists in comparing the mixture in the burner, which is drawn into one cell, with a standard gas (usually air) sealed in the other cell. Figure 25 shows a photograph of the apparatus as used. The only complication arises from the fact that the composition and conductivity of manufactured gas change from time to time so that a simple calibration of the apparatus with mixtures of air and the gas made at one time will not accurately represent the composition of mixtures of air with the gas made at another time. This difficulty is readily overcome, however, by consideration of the following facts. If A represents the

reading of the instrument when air is in the analyzing cell, G_1 represents the reading when the analyzing cell is filled with one gas unmixed with air, G_2 represents the reading when the cell is filled with another gas likewise unmixed with air, and R_1 and R_2 represent the readings when the cell is filled with air mixed with the respective gases in the same proportion in the two cases, the following relation prevails.

$$\frac{A-G_1}{A-G_2}=\frac{A-R_1}{A-R_2}$$

From this equation and a calibration curve for a gas giving one scale reading when unmixed with air, it is easy to construct a calibration curve for a gas which gives any other scale reading. If the apparatus is to be extensively used it is advisable to construct a series of calibration curves for gases which give various readings; it is then possible to interpolate between the curves with considerable accuracy for a gas of any conductivity intermediate between the conductivities of gases for which curves were constructed. Only a minute or two is required to sweep out the cell with the gas being used and determine which calibration curve to employ.

For the successful determination of carbon monoxide in products of combustion, certain modifications of the method are necessary. Since the thermal conductivity of carbon monoxide is near that of air, and because of the low concentrations involved, it is impracticable to measure the very small differences in conductivities of the mixtures. The thermal conductivities of carbon dioxide and air, however, are quite different. By passing the mixture to be analyzed through one cell, then through a combustion furnace where the carbon monoxide is burned to carbon dioxide and from there into a comparison cell, greater differences in conductivity can be obtained because of the change in carbon dioxide content. In order to make the apparatus sufficiently sensitive to indicate small percentages (less than a few tenths of a per cent) the cells must be kept at constant temperature in an oil bath and the voltage accurately adjusted.

If the products of combustion contain no combustible constituents, the instrument is balanced at some scale reading (which may be briefly called reading A), which is nearly but not quite independent of the proportion of other constituents. When combustible gas is present, the position of balance changes from A, by an amount B which is proportional to the concentration of combustible present and gives a total reading $A+B$. By reversing the direction of flow of the sample, the gases in the two cells are interchanged and the reading becomes $A-B$. The two readings are compared by taking the difference between them. This is $2B$ and is independent of changes that affect only A.

It is essential when using the apparatus in this manner to have a sample which does not change during this comparison, hence, continuous sampling is not permissible.

From the carbon monoxide unit the gas passes directly into the analysis cell of the carbon-dioxide unit. The comparison cell of this unit is filled with air and hermetically sealed.

A sampling apparatus and gas circuit for this purpose are shown diagrammatically in Figure 26. The gas sample enters through tube *1*, bubbles through the concentrated sulphuric acid to remove

the moisture, and passes to the filter tower through tube *2*. Before collecting a sample for analysis the line should be well purged. This is accomplished as follows: With the sample bottle full of mercury and stopcock *A* in the position shown in solid lines, purge valve *G* open, and the vacuum valve *F* open, the gas enters as before and leaves the tower by tube *7*. At the T in tube *5* the gas is drawn up and passes through the purge valve and thence to the vacuum line. To collect the sample, the purge and vacuum valves are closed, and stopcock *A* turned to the dotted position. The vacuum valve *F* is again opened and the mercury in the sample bottle is drawn into the reservoir through tube *4*, the gas entering through tube *5*. When the reservoir has been filled and the mercury drawn up into tube *3*, the valves are closed and stopcock *A* turned back to the solid line

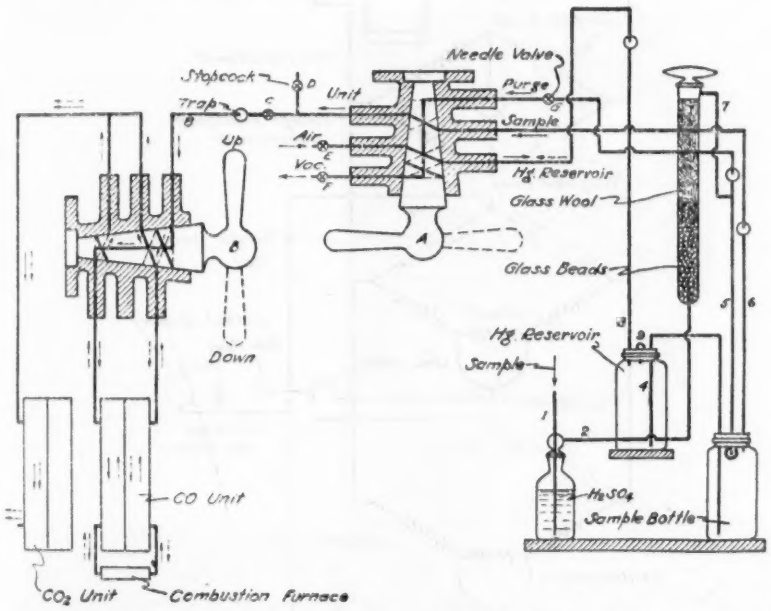

FIGURE 26.—*Flow diagram of apparatus for determining carbon monoxide and carbon dioxide*

position. The sample can now be delivered to the thermal conductivity cells by opening the air valve *E* and line cock *C*. Stopcock *B* is in either the "up" or "down" position. With this arrangement, atmospheric pressure is exerted on the surface of the mercury in the reservoir, thus forcing the gas sample out through tube *6*, stopcocks *C* and *B*, and into the cells. With stopcock *B* in the "up" position, the gas enters the left-hand cell of the carbon-monoxide unit, passes through the combustion furnace, into the right-hand cell, and is discharged from the analysis cell of the carbon-dioxide unit. In the down position, it enters the right-hand cell first and is discharged as before. The solid and dotted arrows indicate the flow for each position. A T and stopcock *C* are placed in the line directly after stopcock *A* so that the sample can be wasted, without going through the units, if desired.

Figure 27 is the wiring diagram of the bridge circuits and Figure 28 is a view of the instrument in use, showing the sampling apparatus on the extreme left.

The apparatus, which has been in continuous use at the Bureau of Standards for the past six years, is sensitive to about 0.002 per cent of carbon monoxide. The determination of carbon dioxide can not be made with quite as great a precision because it is not made by a differential method, but there is no difficulty in making the determination with as great precision and with much greater speed than with any ordinary form of volumetric apparatus.

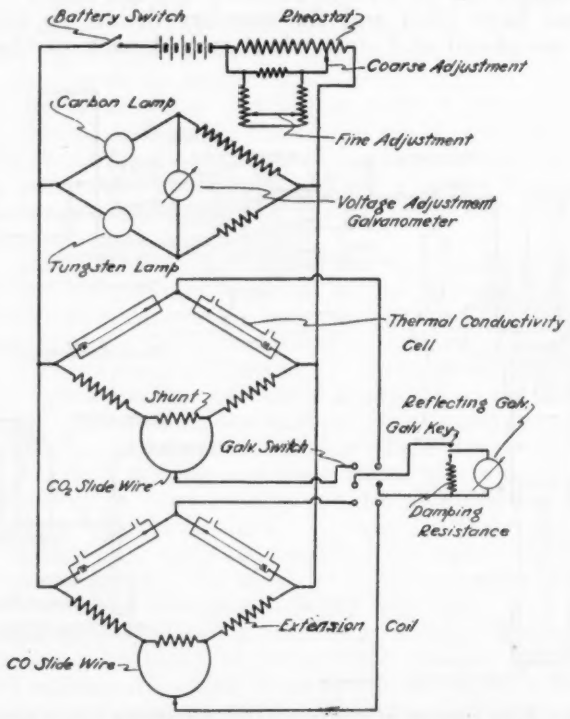

FIGURE 27.—*Wiring diagram of the apparatus for determining carbon monoxide and carbon dioxide*

It should be stated that the effect measured when making a carbon monoxide determination depends not only on the carbon monoxide which is converted to carbon dioxide, but also on any other combustible constitutent which may be oxidized in passing through the combustion furnace. In this method of test hydrogen is the most important of these additional constitutents and is always present when the products of combustion contain carbon monoxide. If the ratio of hydrogen to carbon monoxide remained the same, then the conversion of the scale reading to percentage of carbon monoxide for any unknown sample could be made by means of a calibration curve. Such a curve could be obtained by comparing the readings of the thermal conductivity instrument with chemical determinations of carbon monoxide in the same samples, and when once determined would be

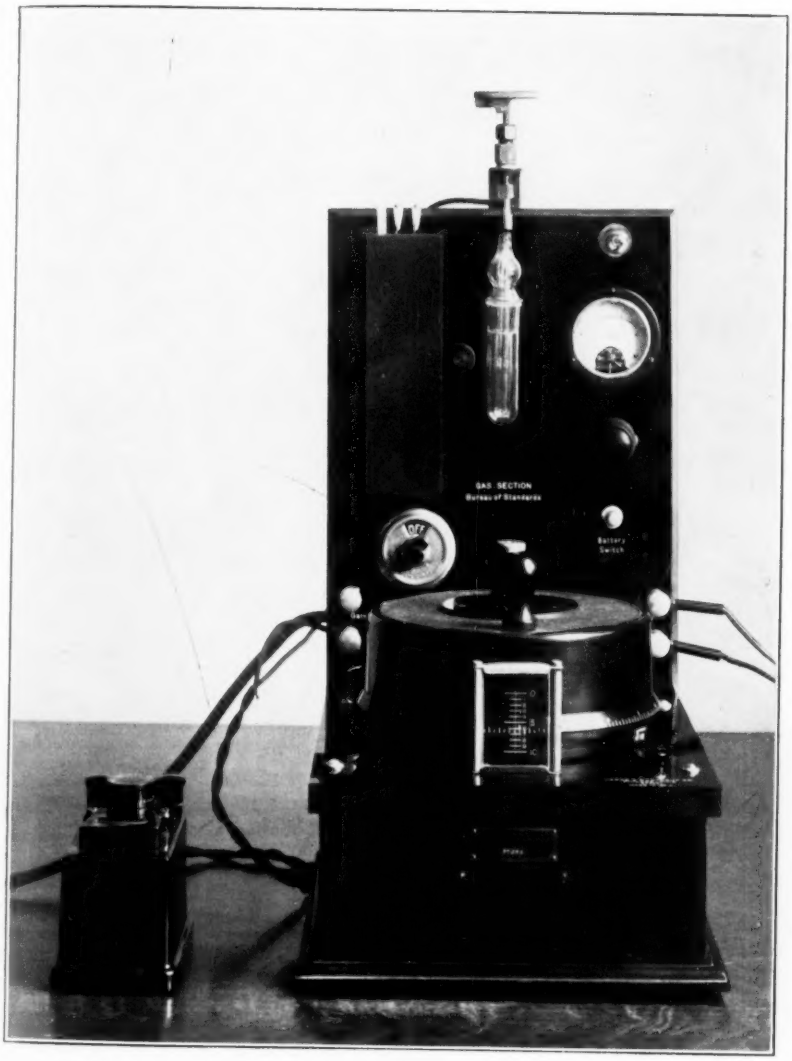

FIGURE 25.—*Air-gas ratio apparatus*

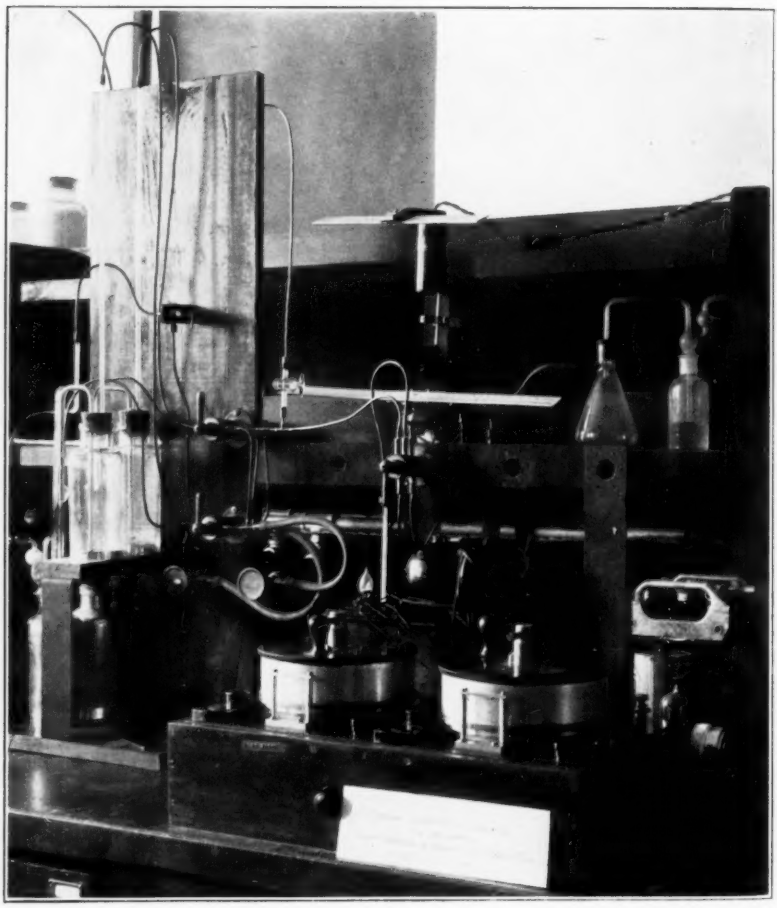

FIGURE 28.—*Apparatus for determining carbon monoxide and carbon dioxide*

applicable to a sample from any fuel gas or type of appliance. Unfortunately, however, the ratio of hydrogen to carbon monoxide does not remain constant, but varies with different mixtures of air to gas and also varies with different appliances. A given scale reading on the thermal apparatus does not, therefore, indicate a definite percentage of carbon monoxide, but a variable amount, depending upon the ratio of hydrogen to carbon monoxide in the sample tested. However, the nearly complete combustion of gas in the presence of fairly high primary air [10] results in a fairly satisfactory calibration curve for amounts of carbon monoxide up to several hundredths of 1 per cent. Smoky flames give low results and the escape of raw gas usually gives high ones.

For the reasons given this method of test is used only where approximate determinations of carbon monoxide are desired, or in tests similar to those described in this paper where the limits of complete combustion ("0 per cent carbon monoxide curves") are required.

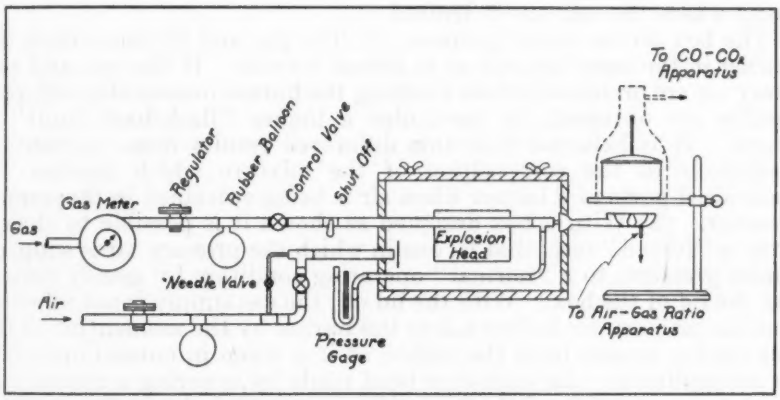

FIGURE 29.—*Diagram of burner testing apparatus*

3. BURNER TESTING APPARATUS USED FOR SUPPLYING VARIOUS ADJUSTMENTS OF GAS AND PRIMARY AIR TO A GAS BURNER

The apparatus used for obtaining the various adjustments of gas and primary air, as well as the arrangement for making efficiency tests, sampling the products of combustion, and the mixture of air and gas within the burner head is shown in Figure 29. The gas after being metered passes through a pressure regulator by means of which it is possible to obtain at the orifice any pressure desired up to the maximum on the line. From the regulator the gas goes through a control valve of the gate type, which is used to obtain a rough pressure setting, the final setting being made by means of the regulator. A plug cock following the control valve permits the gas to be turned off suddenly without changing the adjustment of the control valve and is particularly useful during flash-back determinations. When the flame flashes back into the burner, the gas must be immediately shut off in order to extinguish the gas which will then be burning at

[10] Incomplete combustion results in this case from insufficient secondary air or the loss of heat from the flame before reaction is completed.

the orifice. When the plug cock is again turned on, the original pressure adjustment will be duplicated without any further readjustment and enables a check test to be made more conveniently. From this cock the gas passes directly to the gas orifice and issues into the burner. A connection to a pressure gauge is made just ahead of the orifice. A rubber balloon attached to the line by a T between the regulator and control valve serves to eliminate the pressure fluctuations caused by the gas meter and regulator and produces a steadier flow of gas to the burner.

The air passes through a regulator, past a rubber balloon similar to the one on the gas line, and through two valves into an air-tight box where a baffle placed in front of the inlet breaks up the stream. The air supply to the box is controlled by means of two valves placed in parallel, one gate valve by means of which a rough adjustment is made and the other a needle valve for the final adjustment. The only outlet from the box is through the burner, the mixer of which is securely fastened into the box as shown. The gas and primary air mix in the mixing tube of the burner before reaching the burner ports where the mixture is ignited.

The box serves a dual purpose: (1) The gas and air mix within the burner in the same manner as in actual service. If the gas and primary air are premixed before reaching the burner measurably different results are obtained; in particular a higher "flash-back limit" is found. It is believed that this difference results from momentary variations in the composition of the mixture which reaches the individual ports of a burner when air is being entrained in the normal manner. (2) With a box designed as shown it is possible to change from a "forced" test; that is, one in which the primary air is supplied under pressure, to a "normal" operating condition by merely removing the lid of the box. With the lid off, the gas supply is not affected, but the primary air is drawn into the burner by the momentum of the gas stream issuing from the orifice, as it is when in normal operation in an appliance. An explosion head made by covering a rectangular opening on one side of the box with a piece of shellacked paper protects the gas meter and regulators from possible damage when flash back occurs. Ordinarily, flash back does not damage this paper, but it is a useful safety valve and is easily replaced. A copper sampling tube connecting the burner with the air-gas ratio apparatus permits a sample of the air-gas mixture within the burner head to be taken, and the composition of the mixture to be determined for any given adjustment.

An adjustable grid serves to support a utensil at any desired distance above the burner. When a sample of the products of combustion is desired, a hood designed as shown is placed over the utensil and is supported by the grid. This hood is connected directly to the apparatus for determining carbon monoxide and dioxide by means of copper tubing.

A summary of the various uses which can be made of such an apparatus follows:

1. Any desired mixture of air and gas can be supplied to a burner at any reasonable rate.

2. The exact conditions under which flash back, lifting, or yellow tips occur can be determined for any given burner.

3. It is possible to study the effect on either the efficiency or completeness of combustion of changing such adjustments as gas rate, primary air injection, or distance between burner and utensil.

4. Normal air-injection curves can be obtained by merely removing the lid of the box.

5. The effect of changing pressure on the gas rate can be obtained.

6. The variation of air injection with orifice size or design can be easily determined.

7. By making a complete set of determinations, such as those described in this report, it is possible to compare different gases when using the same burner, or different burners when using the same gas.

WASHINGTON, March 19, 1932.

RP447

THE PHOTOGRAPHIC EMULSION: ANALYSIS FOR NONHALIDE SILVER AND SOLUBLE BROMIDE

By Burt H. Carroll and Donald Hubbard

ABSTRACT

This paper is a critical study of methods proposed for the determination in emulsions of silver in forms other than silver halide, and a description of a new method of extracting soluble bromide from emulsions. The method of Weigert and Lühr, based on double fixation with thiosulphate, is found to be reliable; the principal danger is decomposition of silver thiosulphate to sulphide. The method of Schmidt and Pretschner, direct extraction with nitric acid, is too insensitive. Soluble bromide may be quantitatively extracted from plates by three changes of dilute acid; error from formation of silver-gelatin complex is thus eliminated. Electrometric titration at pH2 or less may be used for liquid emulsions, and is preferable for analysis of plate extracts, but it is also possible in the latter case to determine the bromide by oxidation to cyanogen bromide, with subsequent iodometric titration, according to Lang.

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I. DETERMINATION OF NONHALIDE SILVER

1. INTRODUCTION

The existence in ripened silver bromide-gelatin emulsions of sensitivity nuclei attached to the silver bromide grains is now established so thoroughly that it need not be discussed. The mechanism of their action is outside the scope of this paper. We are here concerned with the methods proposed for the determination of nonhalide silver in emulsions, their reliability and accuracy; and with the evidence on the nature and distribution of the nonhalide silver which is furnished by these analytical methods.

The methods used for the determination of silver liberated on exposure, in attempts (1)[1], (2) to verify the Einstein equivalence equation for photolysis of silver salts in photographic materials, are not sufficiently sensitive to detect nonhalide silver in unexposed emul-

[1] Figures in parentheses here and throughout the text refer to bibliography at the end of the paper.

sions. By extrapolation of the data for silver formed on longer exposures, it has been estimated that photo-silver corresponding to normal image densities is of the order of 10^{-8} part of the total silver (3). The assumption that the sensitivity nuclei represent a fraction smaller, if anything, and quite beyond the reach of analysis, has been commonly made. The data of Sheppard (4) on sensitization by allyl thiocarbamide demonstrated that much higher proportions could be converted to silver sulphide at optimum conditions for sensitization, but there was no proof that all of this was necessarily effective. The analytical determination of nonhalide silver in unexposed developing-out emulsions was first announced by Weigert and Lühr (5). Their results showed a steady increase in the "Ursilber" of silver chloride and bromide emulsions during ripening, as is to be predicted if it is the product of this process. The amount of nonhalide silver was greatest in silver chloride emulsions, and least in those made with silver iodide; in the iodide emulsions it remained practically constant during ripening, in contrast to those made with the other halides. The absolute amounts of nonhalide silver were in all cases far above those for photo-silver corresponding to normal exposures.

In subsequent contributions (6), (7), (8) Weigert and Lühr have given full details of their methods and results. Their results have unfortunately been reported entirely in terms of weight of silver per unit plate area; as the results of other investigators have also been given in somewhat arbitrary terms, we have reduced everything to the common basis of the atomic ratio of nonhalide silver to the total silver in the emulsion. Weigert and Lühr's experimental emulsions were coated at 4.1×10^{-4} g equivalent AgBr per 100 cm^2 of plate; for commercial emulsions we have taken Eder's (9) average value of 9×10^{-4} for German plates. The Ag/AgBr ratio for commercial plates was approximately 2×10^{-4}; in experimental pure bromide emulsions it was 1.5 to 4×10^{-4} depending on the time of ripening.

Weigert and Lühr's procedure is based on the elimination of silver halide by fixing with sodium thiosulphate and washing, and analysis of the silver remaining in the emulsion film. The great increase in sensitivity over previous methods based on the same principle was obtained by differential electrometric titration of the silver with very dilute iodide solution. After fixing and washing, the emulsion film was scraped off the plate (9 by 12 cm) and boiled for five minutes with 0.8 ml of nitric acid, specific gravity 1.2, to break down the gelatin. The solution was then made up to 25 ml with the addition first of 1 ml of concentrated ammonia, next 0.5 ml glacial acetic acid, leaving it faintly acid. The prepared solution was divided between two crucibles, each provided with a silver electrode and a mechanical stirrer; the cell was completed by a salt bridge filled with agar jelly containing potassium nitrate. Potential differences between the electrodes were determined by connecting the cell directly to a highly sensitive galvanometer and reading the throw of the instrument after 30 seconds. The cell was short circuited between readings. In making the titration, iodide solution was added from separate burettes to each of the vessels, one being kept in excess by a small amount, usually 0.1 ml. Using 0.0001 *N* KI, the method was sensitive to 1×10^{-6} gram silver. Careful control determinations established that if the gelatin was broken down by the above procedure it caused no interference, and that the attack of the solution on the electrodes

was negligible. Lühr noted that the first titration with the electrodes after they had been out of use for some time was generally low.

In the earlier part of their work, Weigert and Lühr simply fixed the plates in an alkaline thiosulphate bath [2] and washed thoroughly before stripping and analyzing. Experiments on plates coated with plain gelatin and bathed in fixing baths containing silver indicated that there was a blank of approximately 1×10^{-6} g equivalent of silver per g of gelatin, which could not be removed by washing after such treatment. They accordingly altered their procedure by the addition of a second fixing and washing after the first treatment; in view of the common practical use of double fixation to eliminate the last traces of silver salts from photographic materials, it is somewhat surprising that this had not been used in previous analytical methods depending on thiosulphate fixing. With this modification the blanks approached the limit of error of the titration. They lay considerable stress on thorough washing of the plates between the two fixing baths, reasoning that the removal of the silver held by the gelatin will be more complete as the ratio of sodium thiosulphate to silver thiosulphate is increased and that the optimum condition for use of the second bath is accordingly after the silver salts have been removed as far as possible by water. Their data show a decrease in the silver with increasing time of washing between the fixing baths. In some cases it reached an apparently constant value after washing for four hours, but more frequently there was an appreciable further decrease when the washing time was extended to five hours. In the case of ripened emulsions there is little room for doubt that there was a real quantity of silver much larger than the uncertainty of extrapolation to theoretically complete washing. A standard time of four hours was finally adopted.

Weigert and Lühr recognized that there is loss of silver during the fixing and washing processes since the solutions contain dissolved air, and any oxidation of the very finely divided metal will be followed by solution of the oxide in the thiosulphate. They tested the effect of from 2 to 10 successive fixing baths, 10 minutes each, on a ripened emulsion, the decrease in silver being very considerable with the larger numbers. The loss was less in 5 than in 20 per cent solution; after experiments with more dilute solutions, 5 per cent thiosulphate was adopted for the second fixing bath. We are unable, however, to find that Lühr determined the loss when plates containing known amounts of colloidal silver were given the standard treatment—10 minutes in alkaline 20 per cent thiosulphate, 4 hours washing in running tap water, 10 minutes in alkaline (?) 5 per cent thiosulphate and further washing. This was done with plates containing colloidal silver sulphide in quantities similar to the "Ursilber" of ripened emulsions; the loss, while probably real, was within the limits of error of the procedure.

It is obvious from the nature of the analytical procedure that the "Ursilber" would include both the silver sulphide and the metallic silver present in the emulsion. Weigert and Lühr came to the conclusion that it was almost entirely silver, because the "Ursilber" was greatly diminished by treatment with persulphate. In control

[2] A reference to the work of Chapman Jones on the attack of fixing baths on the developed image indicates that the bath contained 200 g $Na_2S_2O_3.5H_2O$, 5 g Na_2SO_3, and 1 g Na_2CO_3 per liter, but we have been unable to find an explicit statement as to the amount of alkali.

experiments with colloidal silver sulphide in gelatin, persulphate failed to dissolve silver sulphide. These results are directly contradicted by Sheppard (10) in a recent communication in which he reports that known silver sulphide nuclei in emulsions were completely destroyed by persulphate. These emulsions were found also to contain silver in amounts somewhat smaller than the silver sulphide.

Weigert and Lühr's results have been attacked (11), (12), (13), principally because of the use of thiosulphate fixation, which other investigators had found to leave appreciable blanks depending on conditions such as the thickness of the emulsion film. These criticisms are answered by the use of the second fixing bath, in so far as they are based on the adsorption of silver thiosulphates by the gelatin. The very erratic results obtained by Arens and Eggert (12), using Weigert and Lühr's method, appear to reflect more on their experimental technique than on the method. Kieser (13) has pointed out that silver in the quantities reported (Ag/AgBr = 1 to 10×10^{-4}) might be detectable by its color; this also applies, however, to silver sulphide produced by sensitizers like allyl thiocarbamide, and it is not excluded that it actually would be visible by refined methods of comparison.

Shortly after Weigert and Lühr's first communication, Schmidt and Pretschner (14), working independently and by an entirely different method, reported the presence of excess silver in unexposed emulsions. Their values, reduced to the same basis, were about two or three times those obtained by Weigert and Lühr; for fast bromiodide emulsions, Ag/AgBr = 8 to 9×10^{-4} by one method, 2 to 3×10^{-4} by the other. Like Weigert and Lühr, they found that the amount of nonhalide silver increased with the solubility of the silver halide present in the emulsion and could not be correlated with the photographic properties of the emulsion. This apparent confirmation of Weigert and Lühr's results turned out to be accidental. Schmidt and Pretschner worked with large quantities of emulsion (about 0.7 kg) in the "noodles." The emulsion was thoroughly washed in tap water, followed by about 24 hours in changes of distilled water. It was then digested with nitric acid, 3 per cent of the total volume, which broke down the gelatin and coagulated the silver halide, and the silver in solution determined by very carefully corrected precipitation as silver chloride. Schmidt and Pretschner at first apparently considered that the silver determined in this way was present as metal. They later found (15) that on centrifuging emulsions the larger part of it remained in the gelatin, in contrast to photo-silver which was carried out with the silver halide of exposed emulsions. Further experiments (16), (17), (18) on sedimentation and on fixing silver chloride emulsions with sodium sulphite led them to the conclusion that most of the excess silver was not metal, but in some way combined with gelatin. Their final conclusion (19), (20), which we believe to be essentially correct, was that the excess silver was formed during washing by hydrolysis of the silver halide. They ascribed this, however, to the difference in rate of migration of the silver halide ions, which can not account for the results. The present authors in a preliminary note (21) have pointed out that the combination of silver ion with gelatin is responsible for this reaction; quantitative verification of this is given in our communication on the silver ion-gelatin equilibrium (22).

Sheppard (3) has recently reported the application of colorimetric determination of traces of sulphur compounds (23) to the determination of silver sulphide in the silver halide grains centrifuged from ripened emulsions. These results show the predicted increase in $Ag_2S/AgBr$ ratio with increasing specific surface of the grains (although it is noteworthy that the "medium" size grains have a distinct minimum, indicating that the "large" grains, first formed in the precipitation, reduced the concentration of labile sulphur compounds before the others were formed). They constitute an entirely independent confirmation of the existence of nonhalide silver in unexposed emulsions in the quantities first reported by Weigert and Lühr.

Our interest in the subject was primarily in connection with the determination of soluble bromide in emulsions. If there existed nonhalide silver in such quantities as were reported by Schmidt and Pretschner, this might well interfere with analysis for small amounts of bromides. Determination of nonhalide silver is also of use in any experiments on ripening and on nuclear sensitizers, although it is obvious from the available evidence (3) that the quantity is less important than its structure and relation to the silver halide grains. Being distinctly skeptical at first of the reality of the silver determined by any of the methods, we not only considered those published, but attempted independent verification by other processes which will be very briefly reported.

2. EXPERIMENTS WITH THE WEIGERT AND LÜHR METHOD

For the necessary electrometric titrations we used the apparatus which has already been described in another connection (22) measuring the emf of a cell consisting of the silver electrode in the solution to be titrated and a 0.1 N calomel electrode connected to it by a salt bridge filled with ammonium nitrate solution. While our procedure was not strictly a differential titration, the end point was always determined by a plot of $\Delta E/\Delta v$ against volume of solution. The procedure, involving the use of a potentiometer, is somewhat slower than that of Weigert and Lühr, but we found it a real advantage to be able to judge from the constancy of the potential whether the electrode was in equilibrium with the solution. Sluggishness which is completely negligible for the titration of 20 ml of 0.1 N solution is an entirely different matter when the end point comes at 1 ml of 0.00020 N KI. Like Clark (24) and Lühr (7), we found that the electrodes were more satisfactory after use; in fact, the first titration with dilute iodide solutions was quite unreliable. Unlike Lühr, we found it tended to be high rather than low; this is probably because the electrode after cleaning was usually made anode in dilute KI solution. All the experiments were made with 5 by 7 inch plates. Fixing and washing were carried on in new enameled trays, which were discarded when there was any indication of attack on the glaze, or in glass trays. In working with machine-coated experimental plates, the quantity of silver halide on the plate was determined by digesting the fixing baths with zinc. The resulting mixture of silver, silver sulphide, and excess zinc was dissolved in nitric acid and titrated with standard thiocyanate solution, using ferric alum as indicator.

We will, for convenience, refer to the quantity of silver halide per given area as the "coating thickness" of the plate; this quantity is, for a given emulsion, proportional to thickness although it is determined in terms of silver.

By presenting our results in an order quite different from that of the experiments we may develop the subject more logically and economize space. Table 1 gives the data for recent analyses of emulsions to which known amounts of colloidal silver and silver sulphide had been added. The reproducibility of the results for all but the controls was better than 5 per cent, and the values found agree with the amounts added within 12 per cent; in view of the uncertainty of measuring the volumes of emulsion used in making the knowns, the agreement with the true value may be better than this. The knowns were made by mixing the colloid with the emulsion just before coating, control batches being coated without such addition. The colloidal silver had been made by the dextrin method of Carey Lea as modified by Wiegel (25), and purified by two alcohol precipitations; the amounts given are corrected for the traces of silver salts present. Colloidal silver sulphide was prepared by adding first 2.34 ml of 0.107 *M* $Na_2S_2O_3$, then 5.0 ml of 0.100 *M* $AgNO_3$ to 170 ml of warm 1 per cent gelatin solution; the mixture was allowed to stand about an hour before use to complete the decomposition of the silver thiosulphate. The emulsions were not fully ripened, to keep down the nonhalide silver in the control; they were stabilized by adding 10 KBr per 1,000 AgBr before coating, and the analyses were made within two or three days after drying.

TABLE 1.—*Analysis by modified Weigert and Lühr method of emulsions containing known amounts of colloidal silver or silver sulphide*

Emulsion type	Colloid	Silver halide on 5 by 7 inch plate, gram equivalent $\times 10^{-4}$	Nonhalide silver on 5 by 7 inch plate, gram equivalent $\times 10^{-7}$	Ag/AgBr $\times 10^{-4}$ found	Mean difference from control	Ag/AgBr $\times 10^{-4}$ added
Ammonia process, pure bromide.	Control	13.2	0.96	7.3		0
		12.0	.52	4.2		
	Carey Lea silver	15.7	4.40	27.9	23.1	24.9
		17.5	5.24	29.9		
Neutral process, 3.4 mol per cent AgI.	Control	12.3	.48	4.2		0
		12.4	.56	4.5		
	Carey Lea silver	13.1	4.24	32.4	28.7	26.0
		12.3	4.16	33.8		
	Silver sulphide	13.7	4.88	35.6	30.4	34.5
		15.3	5.20	34.0		
	do	14.1	2.30	16.3	12.4	13.8
		13.7	2.36	17.2		

In these experiments we used a modification of the procedure recommended by Weigert and Lühr. The plates were first fixed for 10 minutes in a solution containing, per liter, 300 g $Na_2S_2O_3 \cdot 5H_2O$, 5 g Na_2SO_3 and 1 g Na_2CO_3; this was followed by two changes of a solution containing, per liter, 50 g $Na_2S_2O_3 \cdot 5H_2O$, 5 g Na_2SO_3, and 1 g Na_2CO_3, for five minutes each; the trays were rocked continuously during fixing, and all solutions were kept at less than 20° C. After fixing, the plates were washed for four hours in running tap water at 10° C., stripped, and titrated as already described.

This procedure was adopted in order to maintain at all times a high ratio of soluble thiosulphate to silver. Silver thiosulphate is very unstable unless this condition is fulfilled, and in our opinion the considerable positive errors found by Schmidt (26) and others in the analysis for nonhalide silver by a single fixation are caused more by precipitation of silver sulphide than by adsorption of silver compounds by gelatin. Kieser (27) has demonstrated that, on dissolving silver bromide in thiosulphate solutions after exposure to light, silver sulphide may be found in the residue. In some cases the results for silver may be high, indicating that in addition to conversion of the photolytic silver to sulphide, there may be a precipitation of silver sulphide on the former. Furthermore, our data (22) on the combination of silver ions with gelatin indicate that the amount of silver per gram of gelatin which was found by Weigert and Lühr after a single fixation corresponds at pH 7 to a silver ion concentration of 10^{-6} N, which could hardly exist after four hours of washing. Adsorbed silver would at least be partly removed by extraction of the gelatin with acid, but when plates were fixed and washed by the original Weigert and Lühr procedure, then extracted three times with 0.005 N H_2SO_4 before stripping, no trace of silver could be found in the acid extract and the silver found in the stripped emulsion was not decreased.

Weigert and Lühr determined the blank on their procedure by coating plates with gelatin containing silver bromide dissolved in sodium thiosulphate. Blank emulsions for this purpose are somewhat difficult to prepare. Any emulsion in which silver nitrate solution has been even in momentary contact with gelatin may contain silver or silver sulphide. If the silver bromide is precipitated from aqueous solution with excess of bromide and then emulsified in gelatin, this objection is avoided, but the emulsion is liable to contain lumps which fix too slowly. The most satisfactory process is that originally suggested by Abegg and Hellwig (28), the silver bromide (plus iodide) being dissolved in a hot strong solution of a soluble bromide, and precipitated by diluting this with gelatin solution. The high concentration of soluble bromide liquefies the gelatin, so that we found it desirable to centrifuge the resulting emulsion and resuspend in fresh gelatin. The soluble bromide present was still much higher than normal so that the possibility of reaction of the silver halide with gelatin was minimized. Emulsions prepared by this procedure and coated in commercial thickness (15×10^{-4} g equivalent on a 5 by 7 inch plate) showed no nonhalide silver whatever in quadruplicate analyses by the modified method just described, demonstrating that the results with normal emulsions can not be ascribed to silver retained by the gelatin or to silver sulphide from decomposition of silver thiosulphate. It is necessary to specify, however, that the solutions and wash water be kept cool, and that the coating thickness shall not be excessive. Experiments with similar emulsions extracted by the original procedure and washed at higher temperatures (the tap water having been as warm as 30° C.) gave positive values for silver which increased with the temperature and time of washing.

Schmidt and Pretschner (26) reported that the nonhalide silver found after a single thiosulphate fixation and washing increased with increasing coating thickness of the plate. The original and modified Weigert and Lühr procedures were therefore tested for their dependence on this variable. The results are presented in Figures 1 and 2 by

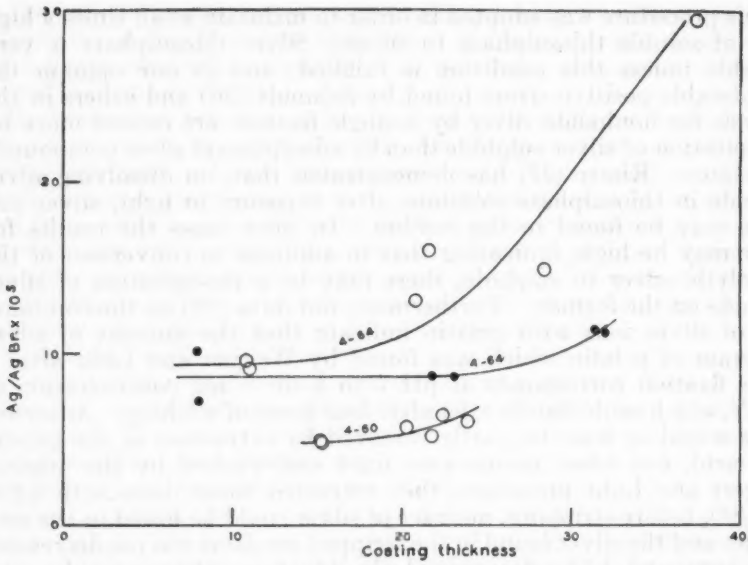

FIGURE 1.—*Variations in the results of determinations of nonhalide silver in plates with varying thickness of emulsion coating*

The data are for experimental emulsions 4–60 and 4–64
(.) Determinations by the original Weigert and Lühr method
(○) Determinations by the modified Weigert and Lühr method

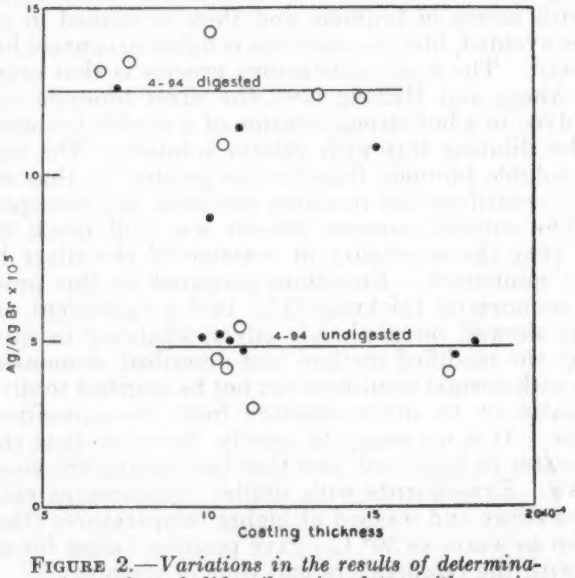

FIGURE 2.—*Variations in the results of determinations of nonhalide silver in plates with varying thickness of emulsion coating*

The data are for experimental emulsion 4–94.
(.) Determinations by the original Weigert and Lühr method
(○) Determinations by the modified Weigert and Lühr method
Note also the increase in nonhalide silver produced by digestion

plotting the nonhalide silver/silver halide ratio against the coating thickness (in terms of g equivalents of silver halide per 5 by 7 inch plate). If the results were independent of the coating thickness, the plot should be a horizontal straight line; an increase in the ratio indicates that the results are not independent of coating thickness. The scattering of the points about the curve also indicates the reproducibility of the methods. Three emulsions were analyzed by the original[3] procedure and four by the modified. Emulsion 4–94 (Fig. 2) was prepared especially for these tests; one-half was coated with the minimum of digestion after washing, the other after two hours, digestion at 55° C. Each half was coated at several thicknesses. The difference in nonhalide silver produced by digestion is obvious.

The reproducibility by the two procedures is about the same; random variations of ± 20 per cent were encountered in some cases. This is not quite as good as the results obtained by Lühr, but is of the order of the systematic errors of the method. The coating thickness did not affect the results up to a value of about 0.15 g AgBr per 100 cm^2 (18×10^{-4} g equivalent per 5 by 7 inch plate); this is the maximum which we have found on commercial emulsions. Thicker coatings, which were found on some of the experimental plates, introduce a positive error; the original procedure was the better of the two in this respect, but either one became unreliable.

Having established the order of accuracy and reproducibility of the analytical method, the next consideration is the evidence concerning the nature of the nonhalide silver in photographic emulsions which may be derived from further study.

It is interesting to find that the Weigert and Lühr procedure gives correct results for colloidal silver in an emulsion, even though the thiosulphate solutions, which are of course saturated with air, attack the same colloidal silver under other conditions. Some of our first tests of the method were made by adding colloidal silver to gelatin and coating on plates so that the gelatin and silver corresponded to the quantities of gelatin and nonhalide silver in emulsions. When these plates were put through the fixing baths and washing, the loss of silver was 30 to 90 per cent, being less for larger amounts of silver. This applied both for Carey Lea silver (the same sample used in the emulsions of Table 1) and for argyrol, losses in the latter case being corrected for the silver proteinate present. It has been suggested (27) that colloidal silver in the emulsion would be converted during fixing to silver sulphide. This would explain the failure of the fixing baths to attack colloidal silver when present in an emulsion, since, in agreement with Weigert and Lühr, we found that the attack on colloidal silver sulphide was small even when it was coated in plain gelatin.

Although the method may give correct results for colloidal silver present in emulsions, we can not agree with Weigert and Lühr that this is the main component of the nonhalide silver ("Ursilber"). We found, in agreement with Sheppard (10), that colloidal silver sulphide is attacked by persulphate. The data are given in Table 2. The silver sulphide was prepared by the decomposition of silver thiosulphate, as described on page 716, and diluted with 6 per cent gelatin solution to the desired concentrations before coating. It is evident

[3] Except for the use of 300 g thiosulphate per liter.

from the data that this same sample was not seriously attacked by thiosulphate solutions. The persulphate solution was 0.10 N $(NH_4)_2S_2O_8$ and 0.10 N H_2SO_4, acting for one hour at 20°, without subsequent washing.

TABLE 2.—*Attack on colloidal silver sulphide by thiosulphate and by persulphate*

(All results expressed as gram equivalents of silver × 10^7 per 5 by 7 inch plate)

Original amount	Residue	
	After modified Weigert and Lühr treatment	After persulphate treatment
4.26, 4.24 9.76, 9.76	3.04, 3.24 9.74, 9.26	1.3, 1.0 1.14, 1.74

The quantity of nonhalide silver found in emulsions has been one of the principal objections to its identification with the sensitivity nuclei. Even unripened and insensitive emulsions contain amounts much larger than is necessary ((29), Tables 29, 30, 31) under favorable conditions to multiply their sensitivity manyfold. We accordingly suggested the hypothesis that most of the nonhalide silver had been formed by reactions involving silver ions or silver-gelatin complexes, while the sensitivity nuclei were formed by rearrangement of compounds first adsorbed to the grains. We have since realized that this may be tested experimentally, as the two classes can be separated by centrifuging the emulsion, and determined by analyzing the silver halide grains and the cleared gelatin. Three emulsions were made up for this purpose. Portions of each were coated unchanged. The rest of the emulsion was separated in the centrifuge, and the cleared gelatin coated in the same way, at about the same thickness, as the original emulsion. In two cases the separated silver halide was again emulsified in fresh gelatin and coated like the rest. The plates were analyzed by the modified method; the coating thickness was excessive, but there are no indications of difficulty from this source. The data in Table 3 clearly demonstrate that the nonhalide silver is associated with the grains and not dispersed through the gelatin. The data given by Sheppard (3) for the silver sulphide in emulsion grains, obtained by a different analytical method, are obviously proof of the same point. The explanation of the existence in the same emulsion of silver sulphide of widely varying effectiveness in sensitizing remains to be provided. It is obvious that some other function of the silver sulphide is overwhelmingly more important than its total quantity.

TABLE 3.—*Distribution in emulsions of nonhalide silver determined by the Weigert and Lühr method*

Type of emulsion	Coating on plate	Total silver on plate, gram equivalents $\times 10^4$	Nonhalide silver on plate, gram equivalents $\times 10^7$	Ag/AgBr $\times 10^5$
Neutral, pure bromide	Original emulsion	22.6	1.88	8.3
		21.8	1.42	6.5
	Cleared gelatin	.1	.4	----------
		.1	.3	----------
	Silver bromide in fresh gelatin	23.6	2.24	9.5
		24.0	2.12	8.9
Ammonia ripened, 1 per cent AgI	Original emulsion	17.3	4.80	27.7
		15.8	4.34	27.4
	Cleared gelatin	.2	0	----------
		.2	0	----------
	Silver halide in fresh gelatin	21.6	7.5	34.7
		21.1	6.16	29.2
	Original emulsion	34.2	2.78	8.1
		33.5	2.68	8.0
	Cleared gelatin	.3	0	----------
		.3	0	----------

3. EXPERIMENTS WITH OTHER METHODS

(a) DIRECT EXTRACTION WITH NITRIC ACID

Direct extraction with nitric acid as recommended by Schmidt and Pretschner, dissolves silver in every form likely to be present except the halides. Soluble halides must be completely removed or they will react with the dissolved silver. The extensive washing necessary to remove the halides results in the formation of silver-gelatin compounds if the washing is done with pure water, with consequent positive errors many times the quantities to be determined. As Schmidt and Pretschner have recognized this, it will be unnecessary to present all the data accumulated to prove the point.

The apparatus for electrometric titration being available, we substituted this for the gravimetric methods of Schmidt and Pretschner, and worked with the emulsion from a 5 by 7 inch plate instead of with larger quantities as "noodles." The sensitivity of the titrations was less than those for the Weigert and Lühr method; the final solution being saturated with silver bromide, it is necessary to titrate with bromide solution and the end point is less sharp because of the greater solubility of silver bromide. The uncertainty of a titration was about 2×10^{-7} g equivalent of silver, as against 0.4×10^{-7} with iodide. The coating thickness of the plates was readily determined by an application of the Liebig method for cyanides. The coagulated silver bromide was filtered off after the nitric-acid digestion, and dissolved in standard sodium cyanide solution. The excess cyanide was then titrated with silver nitrate solution, using the appearance of turbidity as the end point.

The principal systematic error in the determination of nonhalide silver in emulsions by nitric-acid extraction is caused by the formation of silver-gelatin compounds while extracting soluble bromide. This may be eliminated by extracting the bromide with dilute acid instead of with water, as will be explained in more detail in the second part of this paper. However, the sensitivity of the method is insuffi-

cient. The changes in nonhalide silver produced by after-ripening could be detected, but were little larger than the uncertainty of the titration.

Nitric acid extraction was used in the determination of silver-gelatin compounds in emulsions; these results will be given in the second part of this paper.

(*b*) CYANIDE FIXATION

If an unexposed and undeveloped plate is fixed in a cyanide solution under ordinary conditions, followed by adequate washing, all silver will be removed; even silver sulphide will be dissolved by complex ion formation, and small amounts of finely divided silver will be attacked by the dissolved oxygen in the solution and then dissolved by the cyanide. If oxygen were quantitatively removed from the solutions, it might be possible to fix with cyanide, thus removing silver halide and sulphide, and to determine the remaining metallic silver. An apparatus was built in which it was possible to free a liter of water from dissolved gases by refluxing in vacuum for several hours; portions of this water were then transferred to a tube containing the strip of plate to be analyzed, and solid sodium cyanide. The cyanide solution thus prepared in the absence of oxygen fixed the plate and was replaced by successive portions of water. The whole apparatus could be rocked to insure agitation. The attack on silver was tested by using a strip of plate coated with colloidal silver (free from silver salts) in gelatin, 3.3×10^{-6} g equivalent Ag. Using single fixation followed by four changes of water, no silver could be detected in the acidified extract from one run; in a second run where some leakage of air into the apparatus had occurred 3×10^{-7} g equivalent of silver was found in the extract. Complete removal of silver from the emulsion was found to require more thorough washing. Test strips of Eastman 33 plates were fixed in the apparatus in two changes of cyanide solution (a second portion of the solid salt being held out of contact with the solution during the first fixation), followed by six changes of water. No silver could be detected in the remaining emulsion. The method was abandoned at this point as too cumbersome and uncertain.

If the emulsion is freed from soluble bromide and then fixed in air, all silver is extracted, provided the amount present as metal is small. If the fixing bath was then acidified and evaporated to remove hydrocyanic acid (using a hood for this operation), it was found by experiment that silver sulphide and silver halides were precipitated quantitatively, but that traces of silver originally present as metal remained in solution. Apparently if silver cyanide was first precipitated, it was decomposed during the evaporation if the quantity was small enough. This method was of possible interest, since it might be a means of determining metallic silver but not silver sulphide. However, it is obviously dependent on removal of soluble bromide, and any silver-gelatin compounds formed in this process appear in solution and can not be distinguished from metallic silver. Attempts to apply the process to the determination of soluble bromide will be reported in the second part of this paper.

Other solvents were also considered. Sulphite unfortunately can be used only for chloride emulsions. Ammonia was reported by Schmidt (17) to give "very disturbing side reactions"; the nature of these will be discussed in a separate communication on hypersensitization by ammonia solutions.

It is possible that the nonhalide silver might be determined in the emulsion after extraction with acid solutions of thiocarbamides, or with thiocyanates, but neither of these methods were tested.

II. DETERMINATION OF SOLUBLE BROMIDE

The determination of soluble bromide in photographic emulsions is of considerable practical interest because of the effect of this constituent on the ripening and after-ripening process, the sensitivity (especially in the presence of sensitizing dyes) and the stability on storage. The analytical problem appears superficially to be very simple, and probably for this reason has received very little mention in the literature.

Since the soluble bromide is at most about 1 per cent of the total bromide, it is obvious that it can be more accurately determined if separated from the silver bromide. The extraction of the soluble bromide from the emulsion is subject to an unexpected positive error from the formation of silver-gelatin complex and consequent decomposition of silver bromide, which leads to high results. The combination of silver ion with gelatin has been quantitatively studied in this laboratory (22). Its existence was independently inferred by Mitchel and Rawling (30). They analyzed emulsions of known composition by coagulating the gelatin and silver bromide and determining soluble bromide in the filtrate. The results were high in bromide by an amount increasing as the excess of bromide over silver was decreased. Chloride emulsions gave a larger error in the same direction, while iodide emulsions were slightly low in iodide recovered, indicating adsorption. Their data are quite consistent with the formation of silver-gelatin complexes in amounts increasing with the silver ion concentration of the emulsions. If the error from this source is eliminated, the remaining problems are the completeness of extraction of the soluble bromide and its determination in small quantities such as are obtained from reasonable areas of photographic materials.

The methods here proposed are based on the use of acid to prevent the formation of silver-gelatin complexes. Electrometric titration has been used in most of the experiments for the determination of soluble bromide in the extracts, and is strongly recommended for this purpose. The acid extracts may, however, be analyzed by other methods.

As the combination of silver ion with gelatin (22) failed to disappear completely at any hydrogen ion concentration which was tested, the conditions under which it became negligible during extraction of bromide from plates were tested directly. Table 4 gives the data for the extraction of commercial plates (Eastman 33) with varying concentrations of acid. Five by seven inch plates were used in the experiments, the emulsion on each plate containing $15.4 \pm 0.4 \times 10^{-4}$ g equivalent of silver halide. Three extractions were made with 100 ml portions of acid, rocking the plate for three minutes in each. After the extractions, the emulsion was stripped off and analyzed for nonhalide silver by digestion with 0.5 N HNO_3.

Results are given in terms of the ratio of equivalents of soluble bromide or nonhalide silver per equivalent of silver halide.

TABLE 4.—*Extraction of soluble bromide from Eastman 33 plates, and nonhalide silver in plates after extraction*

Solvent used for extraction	$Br^-/AgBr \times 10^3$	Nonhalide silver, after extraction $Ag/AgBr \times 10^3$	Solvent used for extraction	$Br^-/AgBr \times 10^3$	Nonhalide silver, after extraction $Ag/AgBr \times 10^3$
Water	3.0	[1] 1.47	0.0050 N H_2SO_4	2.03	0.29
	2.9	[1] 1.44			.26
	3.7	[1] 1.46	0.025 N H_2SO_4	2.03	.36
	3.7	[1] 1.46		2.00	.25
0.010 N [2] acetic acid	2.06	.45	0.125 N H_2SO_4	2.05	.23
	2.10	.43		1.99	.25
0.0010 N H_2SO_4	3.80	.51	Chrome alum 10 g/liter	2.02	
	3.80	.45		2.06	.22
	2.24	1.29		2.06	.25
	2.31	1.29		1.97	.24

[1] Determined by direct electrometric titration of acidified stripped emulsion, instead of nitric acid extraction.
[2] Five extractions.

This procedure was found to give complete extraction within the limits of error of the titration of the extracts. For example, successive extracts of the Eastman 33 plates with water were found to be equivalent to the following, in ml of 0.0010 N $AgNO_3$: First, 4.18, 4.0; second, 0.5, 0.5; third, 0.0, 0.0. Using 0.010 N HAc, the combined first extracts from two plates were equivalent to 5.8 ml; the second to 0.51 ml, and the third, fourth, and fifth each to 0.0.

The data on bromide extracted and on nonhalide silver remaining show that a constant minimum is reached with solutions as acid as 0.005 N H_2SO_4 (pH approximately 2.7). The nonhalide silver remaining after extraction with the more acid solutions represents silver sulphide rather than silver-gelatin complex, since it checks the nonhalide silver in these same plates found by the Weigert and Lühr method (mean value 0.21×10^{-3}) which includes only silver and silver sulphide.

The chrome alum solution was tested because it seemed likely to be useful for extracting emulsions with a tendency to loosening from the base; electrometric titration may be made without eliminating the alum, although $\Delta E/\Delta v$ at the end point is smaller. The pH of chrome alum solution, 20 g/liter, is 2.16 by the quinhydrone electrode.

The extraction with chrome alum solution (10 g/liter) was tested on an experimental emulsion to which soluble bromide had been added after a thorough washing. 8.0 ml of 0.111 N KBr had been mixed with half the emulsion, containing 0.16 g equivalent silver halide, giving a ratio $Br^-/AgBr$ of 5.5×10^{-2}. Extractions of plates from the half without added bromide contained 0.0, 0.0, 0.0, 0.1×10^{-3} $Br^-/AgBr$; from the half with bromide the ratios were 5.35, 5.33, 5.56, 5.41×10^{-3}. The difference is within the limits of error in making up the known.

While the above data indicate that relative amounts of soluble bromide in different portions of the same emulsion may be determined by extraction, there remained the possibility that the silver halide grains may carry appreciable amounts of alkali bromide which is irreversibly adsorbed or even in solid solution, and hence not to be removed by such extraction. This could be liberated by fixing the plate. Accordingly, the whole emulsion of Eastman 33 plates was

analyzed by the method of Clark (24). After fixing in two changes of cyanide solution, followed by two changes of distilled water, the silver was reduced by digesting with zinc. The halide solution was filtered and hydrocyanic acid eliminated by boiling with acetic acid. The silver and zinc were dissolved in nitric acid and excess nitric acid driven off by gentle heating. The silver nitrate plus zinc nitrate was then dissolved and the silver and halide solutions made up to known volumes and titrated against each other electrometrically. The ratio Ag: halide thus obtained was 1.004, 1.004, 1.002:1. The error in this method is obviously of the same order of magnitude as the soluble bromide present. It indicates, however, that the adsorbed bromide left after extraction with the dilute acid can not be large.

Repeated attempts were made to determine total soluble bromide, including possible adsorbed material, by a modification of this process. The plates were fixed in 1 per cent NaCN, followed by 0.1 per cent NaCN and two changes of water. Hydrocyanic acid and dissolved silver salts were eliminated by acidifying with sulphuric acid (double the amount necessary to liberate the hydrocyanic acid) and twice evaporating to half volume on the steam bath, after which the solution was filtered and titrated electrometrically. Starting with known amounts of silver nitrate and potassium bromide, the correct value for excess bromide was obtained by this procedure. However, the results with extracts from plates were erratic; and the electrode potentials were unsteady unless the solution were strongly acidified during titration. It was found that extracts from certain samples of gelatin produced very similar results when added to controls, indicating reduction of silver bromide by the combined action of the cyanide and organic extract from the gelatin. It is interesting that other samples of gelatin caused no such trouble. Mitchel and Rawling were able to determine bromide in the presence of gelatin by the Lang method (31), which is based on oxidation of the bromine to cyanogen bromide and titration of iodine liberated by the cyanogen bromide after first removing the excess of oxidizing agent. This method was therefore applied to the solutions from the cyanide fixation. The apparent errors were not as large as those of electrometric titration of these solutions, but the results were not satisfactory by either method.

The Volhard method obviously might be used for the determination of bromide in the extracts if chloride were known to be absent, but this will seldom be the case. The adsorption indicators, such as fluorescein, can not be used for titration of halide against silver in the presence of protective colloids, such as gelatin extracts.

As the Lang method was found by Mitchel and Rawling (30) to work in the presence of gelatin, it was tested for use on the acid extracts from emulsions. The plates were extracted three times with 0.005 *N* H_2SO_4 and the combined extracts neutralized with Na_2CO_3 and evaporated to about 10 ml. One to three ml of sirupy phosphoric acid, 3 ml *N* $KMnO_4$ and 3 ml 0.5 *N* NaCN were rapidly added to each sample, and the flasks stoppered and left to stand for 20 minutes; no loss was caused by increasing the time to 30 minutes. After the oxidation was complete, the excess $KMnO_4$ and MnO_2 were eliminated by adding saturated $FeSO_4$ solution in slight excess, followed by about 1 g solid KI. After a minute the liberated iodine was titrated with 0.001 *N* $Na_2S_2O_3$ solution with starch as indicator.

It seems worth reminding the chemist who has not previously used the Lang method that the final reaction is as follows:

$$BrCN + 2H\cdot + 2I^- = HCN + 2I + H\cdot + Br^-$$

In the presence of organic matter, such as gelatin or gelatin extracts, we found it necessary to increase the amounts of $KMnO_4$ and NaCN and the time of oxidation as indicated, even though Mitchell and Rawling report satisfactory results with 1 ml *N* $KMnO_4$ and 0.5 ml of 0.5 *N* NaCN, the proportions recommended by Lang. Examples are given in Table 5. Results, were slightly low in all cases and unless there is a distinct excess of $KMnO_4$ at the end of the oxidation and sufficient cyanide to insure that the Br goes quantitatively to BrCN, the error is very serious.

Comparison of the Lang and electrometric titrations of extracts from plates is given in Table 6. Values obtained by the Lang method were in all but one case lower than those found by electrometric titration. Interfering material of unknown character apparently was responsible for a loss of over 20 per cent in the determination of bromide from the second emulsion by the Lang method. Results with the other emulsions may be described as tolerable for practical use.

TABLE 5.—*Determinations by Lang method of 10.0 ml of 0.00100 N* KBr *to which was added either 1 g gelatin, or acid extracts from 1 g gelatin*

(Calculated volume of 0.0011 *N* $Na_2S_2O_3$, 18.2 ml)

Added material	*N* $KMnO_4$	0.5 *N* NaCN	Time of oxidation	0.0011 *N* $Na_2S_2O_3$
	ml	*ml*	*Minutes*	*ml*
Gelatin	2.0	0.5	5	11.7
				12.4
	5.0	.5	5	8.0
			+	14.5
	5.0	5.0	5	15.1
			10	15.1
			15	16.5
			25	17.2
Extract	1.0	.5	5	10.8
			5+	11.1
	5.0	5.0	20	17.0
			28	17.6
			35	17.3
			40	17.3

TABLE 6.—*Analysis of extracts from plates (with 0.005 N* H_2SO_4*) by electrometric titration and by Lang method*

Emulsion	$Br^-/AgBr \times 10^3$	
	Electrometric titration	Lang method
Commercial unsensitized No. 1	1.90, 1.93, 1.93	1.91, 2.01.
Commercial unsensitized No. 2	8.99, 8.90, 8.70, 8.79	6.8, 6.8.
Commercial panchromatic	0.96	0.84, 0.84.
Experimental 10–2	7.92, 7.99	7.2, 7.4.

In the case of emulsions before coating, we have found that the direct determination of bromide ion concentration by the silver-silver bromide electrode, using only the potential of the electrode in the emulsion without a titration, is quite satisfactory for control of wash-

ing, digesting, and coating conditions, and is very readily carried out if the apparatus is available. It is also possible to determine the amount of soluble bromide by acidifying the emulsion to pH 2 (approximate) and making an electrometric titration; the normality so obtained will not agree with the concentration of free bromide ions found by the electrode potential because of adsorption, and the combination of silver ions with gelatin. The accuracy of the titration may be illustrated by the figures for emulsion 10–2. This was washed thoroughly, then melted and mixed with KBr solution making it 0.00097 *N*. Electrometric titrations gave 0.000965, 0.00098, 0.00097 *N*. The concentration of the emulsion was by mistake not accurately determined but these titrations correspond to about 7.5×10^{-5} Br/AgBr, as compared to 7.9×10^{-5} by extraction of the finished plates. (Table 6.)

Mitchel and Rawling's method for determination of bromide in the emulsion before coating is based on coagulation of the emulsion by magnesium sulphate and alcohol. The error resulting from the combination of silver ion with gelatin might be eliminated if the emulsion were sufficiently acid when coagulated, but we were unable to secure a satisfactory coagulation at pH 2. The electrometric methods only can be recommended for the liquid emulsion, on the basis of our experience.

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WASHINGTON, April 2, 1932.

INTERNATIONAL COMPARISON OF ELECTRICAL STANDARDS

By G. W. Vinal

ABSTRACT

Extended comparisons were made in 1931 of standards for the international ohm, ampere, and volt as maintained by the national laboratories of Germany, England, and the United States. Prof. Dr. H. von Steinwehr and Dr. A. Schulze, of the Physikalisch-Technische Reichsanstalt, P. Vigoureux, of the National Physical Laboratory, and the author met at the Reichsanstalt in Berlin and made joint experiments with the silver voltameter and in addition compared standard cells and resistances. This work was followed by comparisons of the cells and resistances at the Laboratoire Central d'Électricité in Paris and at the National Physical Laboratory in Teddington. This paper gives in detail the results of these comparisons and shows that there are differences in the values of standard cells and resistances which are large enough to suggest the necessity for a readjustment of the units as maintained by the laboratories. The silver voltameter measurements were in good agreement.

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I. INTRODUCTION

Through the courtesy of the Physikalisch-Technische Reichsanstalt (PTR) at Berlin, extended comparisons were made in 1931 of the standards for the international ohm, ampere, and volt as maintained by

the national laboratories of Germany, England, and the United States. Wire standards of resistance and standard cells were carried by hand to the Reichsanstalt for this comparison. A series of 10 experiments with the silver voltameter was made by representatives of the three laboratories to verify the values assigned to groups of Weston normal cells. Following the measurements in Berlin, the wire resistance standards and standard cells belonging to this bureau were carried to the Laboratoire Central d'Électricité (LCE) in Paris, and to the National Physical Laboratory (NPL) at Teddington, near London, for further comparisons. Two standard cells of the Reichsanstalt were also carried to these laboratories. At the conclusion of the measurements abroad the bureau's coils and cells and the two Reichsanstalt cells were brought to the Bureau of Standards (BS) for further measurement.

The initial and final values for both coils and cells at the Bureau of Standards differed by only a few parts in a million. This fact coupled with the several check measurements at the various laboratories affords highly consistent data by which an accurate estimate of the differences existing between the electrical standards of Germany, France, England, and the United States can be made.

In some respects the cooperative work done at the Reichsanstalt was similar to the work of the International Technical Committee at the Bureau of Standards in 1910. That committee, however, had the duty of recommending a uniform basis of measurement for the international ohm and of determining the value to be assigned to the Weston normal cell on the basis of the ohm and the voltameter measurements, which were made by the delegates. In doing this, the committee was carrying out the mandates of the International Conference on Electrical Units and Standards, London, 1908

The International Technical Committee [1] recommended that the ohm should be based on the mean value of the mercury units of Germany and England. The unit thus defined has since been known as the "Washington unit." On the basis of this unit of resistance and the voltameter measurements the Technical Committee recommended the adoption of 1.0183 volts at 20° C. as the electromotive force of the Weston normal cell. As a basis of measurement this is assumed to be exact to the sixth decimal, 1.018300 volts.

These recommendations of the technical committee were adopted by the International Committee on Electrical Units and Standards, which was then in existance, and by the national laboratories which began using these units on January 1, 1911. A uniform basis was thus provided for electrical measurements. Since then the national laboratories have maintained their standards by wire resistance coils and standard cells as each laboratory deemed best. Recourse to the mercury ohm [2] and silver voltameter [3] has been infrequent and, in general, such measurements have not been used to reassign values to the working standards. This is not a matter of neglect, but rather a tacit recognition of the fact that the units for the ohm and the volt

[1] Report to the International Committee on Electrical Units and Standards, published by Bureau of Standards, M16, 1912.

[2] Die Quecksilbernormale der PTR für das Ohm (Fortsetzung V), von Steinwehr und Schulze, 1927. Determinations by Smith 1912 and Hartshorn 1924. Reports of NPL, p. 40, 1912; p. 93, 1925. Construction of Primary Mercurial Resistance Standards, Wolff, Shoemaker, and Briggs, B. S. Bulletin, vol. 12, p. 375, 1915.

[3] Nachprüfung der EMK des internationalen Westonelements mit Hilfe des Silbervoltameters, von Steinwehr und Schulze, Zeit. f. Instrk., vol. 42, p. 221, 1922.

can be maintained for a reasonable length of time to a higher degree of constancy by suitable wire standards of resistance and standard cells than by frequent experiments with the mercury ohm and the silver voltameter.

Twenty-one years have elapsed since this agreement providing a uniform basis became effective. Intercomparisons of standards of electromotive force between several of the national laboratories in the years 1929 and 1930 indicated significant differences to exist between the standards of this bureau and the Reichsanstalt and lesser differences between the bureau and the National Physical Laboratory. The principal object of the present work, therefore, was to make voltameter measurements at the German laboratory simultaneously with representatives of the other laboratories with a view to explaining these differences. The opportunity for this comparative work came through arrangements previously made between the Bureau of Standards and the Reichsanstalt for an exchange of personnel in the year 1931. Prof. Dr. Henning, of the Reichsanstalt, took part in investigations on the temperature scale at the bureau for a period of about two months and the author spent about the same time in Berlin. Because of the interest of other laboratories in this cooperative investigation, Mr. Vigoureux, of the National Physical Laboratory, came to Berlin, at the invitation of the Reichsanstalt, to take part in the intercomparison.

II. ARRANGEMENTS AT THE P. T. R. FOR THE WORK

The work was done in the Elektrische Abteilung, of which Prof. Dr. Giebe is the director. The laboratory for Elektrische Einheiten und Messungen is in charge of Prof. Dr. von Steinwehr who, with Doctor Schulze, cooperated in the measurements reported in this paper. Others who assisted were Doctor Gremmer, Herr Kessner, Herr Gutmann, and Herr Höft. Grateful acknowledgment is due to these gentlemen and to Mr. Vigoureux, of the National Physical Laboratory, for their friendly cooperation in the course of this work.

The constant-temperature room in which the standard cells are kept and in which the voltameter experiments were made is located in the Observatory Building. An office with laboratory facilities was also provided in this building for the use of Mr. Vigoureux and the author.

By agreement the results are being published by the several laboratories independently after review by the other laboratories which were concerned in the work.

III. COMPARISONS OF STANDARDS FOR THE OHM

Before discussing the results of the voltameter measurements at Berlin it is desirable to present the comparisons of standards for the ohm and volt. Three wire resistance standards of the bureau,[4] which were carried by hand, have been measured by the laboratories at Berlin, Paris, and Teddington. Measurements of these coils at the bureau in May preceding and in October following the measurements abroad are given in Table 1. The mean value for the group of coils

[4] The construction of these coils has been described by Thomas, B. S. Jour. Research, vol. 5, p. 295, 1930.

is identically the same in May as in October, indicating that the coils have suffered no change by being carried to the foreign laboratories. The bureau's values are expressed in terms of the Washington unit as preserved by a group of 10 coils constituting the bureau's primary reference group.

1. AT THE PHYSIKALISCH-TECHNISCHE REICHSANSTALT

The unit employed in 1910 by the Reichsanstalt for certifying resistances to the public was within 5 parts in 1,000,000 of the "Washington unit," agreed upon by the International Technical Committee. Their unit has been preserved by four resistance coils. Occasional comparisons of these coils have been made with mercury tubes, however, and these measurements indicate a gradual increase in the resistance of these coils amounting on the average to about 1 microhm per year. The last comparison[5] with the mercury tubes was in 1923–1925, and the result showed that the unit as preserved by the Reichsanstalt coils is larger than their mercury-ohm unit by 33×10^{-6}. For present international comparisons, the Reichsanstalt has chosen to express the results in terms of "international ohms" based upon their latest mercury-ohm experiments; that is to say, the values of the bureau's coils measured against their coils have been increased by 33×10^{-6}.

Two methods of comparing resistance standards were employed. The first measurements were made by the differential galvanometer method.[6] The second set of measurements was made on the Kelvin bridge.[7]

TABLE 1.—*Comparison of measurements at the Bureau of Standards on resistance coils before and after the measurements abroad*

[Bureau of Standards coils]

Coil No.	Temperature	May, 1931	October, 1931
	°C.	*Int. ohms*	*Int. ohms*
37	20	0.999917	0.999917
42	20	.999823	.999824
54	20	.999457	.999455
Mean		.999732	.999732

NOTE.—The October values confirm the May values, which are used in subsequent tables.

TABLE 2.—*Comparison of resistance coils at the Physikalisch-Technische Reichsanstalt, 1931*

[Measurements on Bureau of Standards coils at 20° C.]

Coil No.	June	July	Mean P. T. R. values	B. S. values (May)	PTR-BS
	Int. ohms	*Int. ohms*	*Int. ohms*	*Int. ohms*	*Microhms*
37	0.999908	0.999908	0.999908	0.999917	−9
42	.999815	.999813	.999814	.999823	−9
54	.999449	.999448	.999448	.999457	−9
Mean difference					−9

NOTE.—The June measurements were made at 20.17°, 20.31°, and 20.39°, respectively, and the results calculated to 20°.

[5] See footnote 2, p. 730.
[6] Geiger u. Scheel, Handbuch der Physik, vol. 6, p. 455.
[7] Idem. p. 452.

TABLE 3.—*Comparison of resistance coils at the Laboratoire Central d'Électricité, 1931*

[Measurements on Bureau of Standards coils at 20° C.]

Coil No.	L. C. E. certificate values	B. S. values	LCE-BS
	Int. ohms	*Int. ohms*	*Microhms*
37	0.999847	0.999917	−70
42	.999753	.999823	−70
54	.999387	.999457	−70
Mean difference			−70

Table 2 gives the measurements on the bureau's coils at the Reichsanstalt and shows that the mean difference between the P. T. R. and the B. S. values is 9 microhms. The P. T. R. values are smaller than the values certified by the bureau, which indicates that the P. T. R. unit is larger by this amount.

2. AT THE LABORATOIRE CENTRAL D'ÉLECTRICITÉ

The wire resistance standards (and cells also) have been measured at the Laboratorie Central d'Électricité through the courtesy of M. Jouaust and M. Picard. The unit of resistance maintained at this laboratory is the Washington unit.

Table 3 gives the results of measurements on the bureau's coils at the L. C. E. The difference from the bureau's standards is 70 microhms. The L. C. E. values are smaller than the B. S. values, indicating that the L. C. E. unit is larger. There have been no previous comparisons of B. S. standards with L. C. E. standards for the past 20 years. A comparison [8] between the standards of the L. C. E. and the P. T. R. was made in 1929 and the results at that time agree with the present measurements to within 8 microhms.

3. AT THE NATIONAL PHYSICAL LABORATORY

Following the measurements in Paris the resistance coils were taken to London for measurement at the National Physical Laboratory. The author is indebted to Doctor Dye and Mr. Vigoureux for their cooperation in these comparisons in which they were assisted by Mr. Watts.

The Washington unit has been preserved at the N. P. L. by four 1-ohm manganin coils which have consistently held the same relative values. Between 1912 and 1930 the relative variation of any one coil from the mean of 4 is stated to be less than 1 part in 100,000. The N. P. L. has, however, chosen for the present international experiments to express its unit for the ohm as the "international ohm" based upon mercury-ohm determinations made by Smith [9] in 1912, and by Hartshorn [9] in 1924. Smith found the Washington unit as preserved by their coils greater than his mercury unit by 16×10^{-6} and Hartshorn found it 41×10^{-6} greater. The laboratory has therefore chosen 30×10^{-6} as a round figure expressing the mean of these two results, and the values here reported for the bureau's coils

[8] A report of these measurements was published in the Rapport, Comité Consultatif d'Électricité, 1930, p. 123.

[9] See footnote 2, p. 730.

are 30 × 10^{-6} greater than the results of measurements in terms of the Washington unit as preserved at the N. P. L.

The method employed for the intercomparison of resistance standards is described in Glazebrook's Dictionary of Physics.[10]

Table 4 gives the results of measurements on the bureau's coils at the National Physical Laboratory. The average difference indicates that the N. P. L. "international ohm" is smaller than the B. S. "Washington unit" by 4 microhms which agrees with the difference calculated from the Berlin measurements (see Table 5) to within 1 microhm.

TABLE 4.—*Comparison of resistance coils at National Physical Laboratory, 1931*

[Measurements on Bureau of Standards coils at 20° C.]

Coil No.	Mean N. P. L. values	B. S. values	NPL-BS
	Int. ohms	*Int. ohms*	*Microhms*
37	0.999924	0.999917	7
42	.999826	.999823	3
54	.999458	.999457	1
Mean difference			4

TABLE 5.—*Summary of resistance coil comparisons, 1931*

[Differences of the measured values in microhms]

Place of measurement	Coils		Comparison	PTR-BS	PTR-NPL	NPL-BS	LCE-BS
	Source	No.					
Berlin	B. S.	3	Direct	−9			
	N. P. L.	3	do		−12		
	BS and NPL	3-3	By difference			+3	
Paris	B. S.	3	Direct				−70
London	do	3	do			+4	
Mean differences				−9	−12	+4	−70

NOTE.—A minus sign means that the measured value at the laboratory first named is less than the measured value at the second. In comparing the magnitude of the unit, however, it is obvious that the larger the unit, the smaller will be the measured value for the coils.

4. SUMMARY OF COMPARISONS OF RESISTANCE COILS

Table 5 gives a summary of all the measurements on resistance coils, including a comparison with three coils of the N. P. L. which were measured at Berlin, but for which the detailed figures are not given in this paper. The maximum difference of the values is 74 microhms, which exists between the French and British laboratories. Since the measured values are larger as the unit is smaller, the differences for the coils as given in Table 5 have been translated into differences in the units and are shown graphically in Figure 1. The larger units in each case are at the top of the figure.

[10] Volume II, p. 717.

IV. COMPARISON OF STANDARDS OF ELECTROMOTIVE FORCE

Comparisons of the standards of electromotive force have been made also at the three laboratories. The standard cells which were carried abroad for these measurements are listed in Table 6. Six of these cells have been brought back to the bureau and remeasured. The differences are slightly greater than in the case of standards for the ohm, but the mean value of the cells which were brought back to

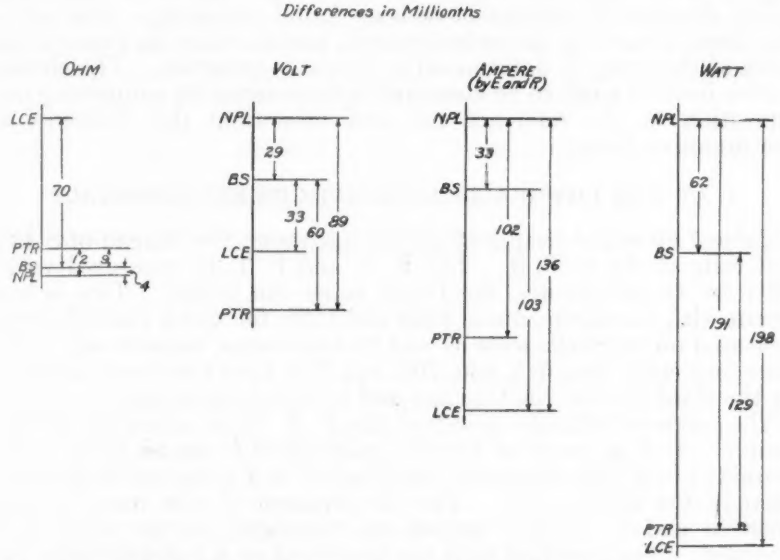

FIGURE 1.—*Relative values of units as found in international comparisons of 1931*

the bureau differs from the mean of the same cells in May by only 2 microvolts.

TABLE 6.—*Comparison of measurements at the Bureau of Standards on standard cells before and after measurements abroad*

[Bureau of Standards cells, 28° C.]

Cell No.	May, 1931	September-October, 1931	Difference	Remarks
	Int. volts	*Int. volts*	*Microvolts*	
685	1.017912	1.017908	−4	
688	1.017883	1.017881	−2	
700	1.017921	1.017918	−3	
714	1.017873	1.017877	+4	N/10 acid cell.
719	1.017951	1.017946	−5	
721	1.017949			Left at P. T. R.
725	1.017948			Left at L. C. E.
726	1.017949			Do.
727	1.017947			Left at P. T. R.
730	1.017951	1.017947	−4	
Mean difference			−2	

The maintenance of the standard for the volt at the Bureau of Standards has been described [11] previously. The primary reference group at the present time consists of 20 cells, 15 of which were made 26 years ago. These cells have shown a remarkable degree of constancy. The group is kept at a constant temperature of 28° C. in an oil bath which is provided with thermostatic control. The value assigned to the average electromotive force of the group corresponds to the value 1.0183 international volts at 20° C. for the Weston normal cell. The electromotive forces of the cells themselves, however, are slightly lower than for Weston normal cells. No corrections for a yearly decrease in voltage have been found necessary. One cell in this group is used as the reference cell, and its value in terms of the mean of the group is determined at frequent intervals. The electromotive force of a cell to be measured is determined by connecting it in opposition to the reference cell and measuring the difference in electromotive force.

1. AT THE PHYSIKALISCH-TECHNISCHE REICHSANSTALT

Table 7 gives the results of measurements on the Bureau of Standards cells at the P. T. R. The B. S. and P. T. R. measured values differ by 60 microvolts, the latter being the higher. This is consistent with measurements in 1929 and 1930, for which the differences measured on four cells were 57 and 60 microvolts, respectively. The same four cells, Nos. 685, 686, 700, and 714, have now been measured for the third time at the German and British laboratories.

The primary reference group of the P. T. R. is called the Kleiner Stamm. It is a group of 10 cells maintained in an oil bath that is contained in a large insulated case located in a constant-temperature room in the observatory. The temperature of this room is quite constant and no further temperature regulation of the oil baths is provided. The standard cells are measured on a potentiometer, one of the cells of the Kleiner Stamm being taken as the reference cell. The 10 cells included in this group are part of a slightly larger group which was brought to the bureau in 1910 by Doctor Jaeger at the time of the international technical committee. The mean value of the whole group in 1910 was found to be the same as the mean of the group means of the cells submitted by the four laboratories at that time and to this mean of the group means was assigned the value 1.0183 volts at 20° C. as representing the Weston normal cell.

Silver voltameter measurements were made by the Reichsanstalt in 1913 [12] and 1921,[13] and these confirmed the figure 1.01830 volts for this group. As a consequence the group has been used up to the present time for international comparisons without change in the assigned value.

2. AT THE LABORATOIRE CENTRAL D'ÉLECTRICITÉ

The bureau's standard cells, with the exception of two which were left at the Reichsanstalt, were taken to Paris and measured at the Laboratoire Central d'Électricité. The values certified by the L. C. E. are given in Table 8. The mean results indicate a difference

[11] Vinal, Trans. Am. Electrochem. Soc., vol. 54, p. 249, 1928.
[12] von Steinwehr, Zeit. f. Instrk., vol. 33, pp. 321 and 353, 1913.
[13] von Steinwehr and Schulze, Zeit. f. Instrk., vol. 42, p. 221, 1922.

in the measured values of electromotive force of the cells amounting to 34 microvolts, the bureau's values being the smaller.

3. AT THE NATIONAL PHYSICAL LABORATORY

The bureau's cells, except two which were left in Paris, were taken to the National Physical Laboratory for measurement. At the N. P. L. a number of standard cells are made each year. The unit which is employed at this laboratory is based on the value 1.018300 for the neutral Weston cell at 20° C. The cells, however, are tenth-normal acid cells and have an electromotive force 62 microvolts lower than the neutral cells. After corrections for acidity and temperature have been made the proper value is assigned to the mean of the groups of cells made during the five preceding years.

TABLE 7.—*Standard cell comparisons at the Physikalisch-Technische Reichsanstalt, 1931*

[Measurements on Bureau of Standards cells, 20° C.]

[Actual temperature during measurement: P. T. R. 19.98° to 20.35° C., B. S. values calculated to 20° C. from measurements at 28° and 25° C.]

Cell No.	June 5	June 12	June 24	June 26	June 30	July 2	July 6	July 9	July 14	July 18	Mean	B. S. values, May 11	PTR-BS	Remarks
											Int. volts	*Int. volts*	*Micro-volts*	
685	1.018352	352	351	348	349	351	352	347	-----	-----	1.018350	1.018292	58	
686	323	323	321	320	321	322	321	326	-----	-----	322	263	59	
700	369	373	371	369	368	368	372	376	-----	-----	371	301	70	
714	317	317	315	313	314	317	317	318	-----	-----	316	253	63	
719	382	-----	-----	-----	-----	-----	391	392	-----	-----	388	328	60	Open circuit repaired.
721	384	382	384	384	383	382	386	381	377	377	382	326	56	Left at PTR
725	383	385	383	383	382	382	383	391	-----	-----	384	325	59	
726	384	382	385	383	383	385	385	389	-----	-----	384	326	58	
727	379	384	387	379	379	380	381	387	376	372	380	325	55	Do.
730	388	389	389	387	386	389	387	388	-----	-----	388	326	62	
Mean	1.018366	365	365	363	363	364	367	369	-----	-----	1.018366	1.018306	60	

TABLE 8.—*Standard cell comparisons at the Laboratoire Central d'Electricite, 1931*

[Measurements on Bureau of Standards cells, 20° C.]

[L.C.E. measurements at 20.0° to 20.7° C.; B.S. values calculated to 20° C. from measurements at 28° and 25°.]

Cell No.	L. C. E. certified values	B. S. values	LCE-BS	Remarks
	Int. volts	*Int. volts*	*Microvolts*	
685	1.018329	1.018292	37	
686	304	263	41	
700	328	301	27	
714	297	253	44	
719	353	328	25	
725	352	325	27	Left at L. C. E.
726	358	326	32	Do.
730	365	326	39	
Mean	1.018336	1.018302	34	

TABLE 9.—*Standard cell comparisons at the National Physical Laboratory, 1931*

[Measurements on Bureau of Standards cells at 20° C.]

[N. P. L. values at 20° C.; B. S. values calculated to 20° from measurements at 28° and 25°]

Cell No.	August 25	August 28	August 29	Mean N. P. L. values	B. S. values	NPL-BS
	Int. volts			*Int. volts*	*Int. volts*	*Microvolts*
685	1.018263	262	261	1.018263	1.018292	−29
686	232	234	233	233	263	−30
700	289	284	283	285	301	−16
714	229	229	228	229	253	−24
719	296	296	295	296	328	−32
730	297	297	296	297	326	−29
Mean	1.018268	267	266	1.018267	1.018294	−27

Table 9 gives the measurements on the Bureau of Standards cells at 20° C., correpsonding in this respect with the measurements made in Berlin and Paris. The difference between the measured values is 27 microvolts, the bureau's values in this case being larger than those of the N. P. L.

Because of the importance of temperature corrections in making these measurements the bureau's cells were also measured at the N. P. L. at 16°, 25°, and 28° C. The results are given in Table 10. It will be observed that the difference between the N. P. L. and the bureau's measurements decreased as the temperature was increased. This can be explained on the theory that the cells do not exactly follow the international temperature formula. For the purpose of the present comparison, however, the measurements at 20° C. were chosen, since this was the procedure followed by other laboratories.

TABLE 10.—*Standard cell comparisons at the National Physical Laboratory, 1931*

[Summary of measurements at N. P. L. on Bureau of Standards cells at 4 temperatures. Results expressed as differences in microvolts.]

Cell No.	At 16° C. NPL-BS	At. 20° C. NPL-BS	At 25° C. NPL-BS	At 28° C. NPL-BS
685	−33	−29	−26	−23
686	−36	−30	−27	−22
700	−29	−16	−23	−23
714 (acid)	−33	−24	−22	−14
719	−38	−32	−30	−26
730	−37	−29	−29	−24
Mean	−34	−27	−26	−22

Comparisons of four bureau cells (Nos. 685, 686, 700, 714) were made at the N. P. L. in 1929 and 1930 at a temperature of 28° C. corresponding to the temperature employed at the Bureau of Standards for the measurement of these cells. The mean difference for these four cells measured at 28° C. agrees closely with measurements of 1929 and 1930 as shown in Table 11.

TABLE 11.—*Comparison of four B. S. cells at the N. P. L. for the years 1929, 1930, and 1931*

[Measurements made at 28° C.]

Cell No.	NPL-BS, 1929	NPL-BS, 1930	NPL-BS, 1931
685 (neutral)	−14	−23	−23
686 (neutral)	−15	−21	−22
700 (neutral)	−9	−15	−23
714 (*N*/10 acid)	−30	−22	−14
Mean	−17	−20	−20

While the mean values for the difference between N. P. L. and B. S. measurements on these cells are very closely the same for the three years, it is noticeable that the individual differences of the neutral cells are increasing with time, but the reverse is true of the acid cell. This supports a conclusion reached at the bureau some time ago on the basis of other evidence that a study of the temperature coefficient of the saturated cell as a function of age is needed.

4. COMPARISON OF FOUR PHYSIKALISCH-TECHNISCHE REICHSANSTALT CELLS

A comparison between the various laboratories has also been made on the basis of measurements of cells belonging to the Physikalisch-Technische Reichsanstalt. Two of these cells were given to the delegate from the National Physical Laboratory and two to the author. The latter cells have been measured in Paris, London, and Washington, the former have been measured in London only.

Table 12 gives the complete results on these cells beginning with measurements made at the Reichsanstalt. These measurements confirm those of the other groups of cells described previously.

5. SUMMARY OF COMPARISONS ON CELLS

The standard cell comparisons are summarized in Table 13 in which it is shown that the measurements at the different laboratories are consistent to a high degree. The four comparisons between the P. T. R. standards and the bureau's standards were concordant to within 1 part in 100,000 although the measurements were made in four different laboratories. The final results have been weighted in accordance with the number of cells in the group. When comparisons were made of two groups the result has been assigned a weight proportional to the smaller number of cells. The minus signs have the same significance in this table as in Table 5. Differences in the unit maintained for the volt in these laboratories are shown graphically in Figure 1. In general, these results are in fair agreement with comparisons reported by Takatsu and Jimbo.[14]

[14] Rapport, Comité Consultatif d'Électricité, p. 119, 1930.

TABLE 12.—*Comparison of four Physikalisch-Technische Reichsanstalt cells at the Laboratoire Central d'Électricité, the National Physical Laboratory, and the Bureau of Standards, 20° C.*

Date and place, 1931	3,116	3,115	3,118	3,117
P. T. R.				
June 5	1.018419	1.018421	1.018417	1.018418
June 12	420	423	418	419
June 24	418	419	415	416
June 26	420	421	418	419
June 30	416	417	414	415
July 2	419	421	416	418
July 6	424	422	419	418
July 9	420	418	419	418
July 14	(414)	(414)	----------	(410)
July 18	(412)	(412)	----------	----------
Mean	1.018420	1.018420	1.018417	1.018418
L. C. E.				
July 28	----------	----------	1.018389	1.018394
July 29	----------	----------	403	405
July 30	----------	----------	390	389
July 31	----------	----------	389	389
Aug. 3	----------	----------	394	392
Mean	----------	----------	1.018393	1.018394
N. P. L.				
Aug. 25	1.018327	1.018325	1.018326	1.018332
Aug. 28	324	326	324	327
Aug. 29	326	327	324	326
Mean	1.018326	1.018326	1.018325	1.018328
B. S.				
Sept. 23	----------	----------	1.018347	1.018352
Sept. 24	----------	----------	349	352
Sept. 25	----------	----------	348	352
Sept. 29	----------	----------	349	352
Oct. 1	----------	----------	349	352
Oct. 2	----------	----------	349	352
Oct. 5	----------	----------	350	351
Mean	----------	----------	1.018349	1.018352

TABLE 13.—*Summary of standard cell comparisons, 1931*

[Differences in microvols,]

Place of measurement	Cells		Comparison	PTR-BS	PTR-NPL	NPL-BS	LCE-BS	LCE-PTR
	Source	No.						
Berlin	BS	10	Direct	60	----------	----------	----------	----------
	NPL	8	----do	----------	90	----------	----------	----------
	BS and NPL	10-8	By difference	----------	----------	−30	----------	----------
Paris	BS	8	Direct	----------	----------	----------	34	----------
	PTR	2	----do	----------	----------	----------	----------	−24
	BS and PTR	8-2	By difference	58	----------	----------	----------	----------
London	BS	6	Direct	----------	----------	−27	----------	----------
	PTR	4	----do	----------	93	----------	----------	----------
Washington	BS and PTR	6-4	By difference	66	----------	----------	----------	----------
	PTR	2	Direct	67	----------	----------	----------	----------
Weighted mean	----------	----------	----------	62	91	−29	34	−24

NOTE.—Weighted according to number of cells.

V. SILVER VOLTAMETER MEASUREMENTS

The silver voltameter measurements occupied most of the time spent at the Reichsanstalt. The deposits were made and weighed in the constant-temperature room in the observatory.

The shipment of the bureau's voltameter apparatus was made by courtesy of the State Department through the diplomatic pouch and delivered to the embassy in Berlin. The bureau's equipment for the silver voltameter included voltameters of both the Smith form and the porous cup form and a considerable amount of silver nitrate which had been carefully purified. The porous cup voltameter was used on only one occasion, however, in the German laboratory.

1. ELECTRICAL CIRCUIT

The electrical circuit is shown diagrammatically in Figure 2. Unlike the arrangements at the Bureau of Standards, the current is allowed to drift, and readings of the potential drop across the standard resistances are taken as changes of 1 part in 100,000 occur. The time of each reading is recorded. At the conclusion of each experiment the time-voltage data are integrated to obtain the average value of the voltage. Integrations have been made by representatives of each of the laboratories and the results are given in Table 14. The concordance of the results indicates that a high degree of precision can be obtained, but it must be assumed that fluctuations of the current during the first minute or two, and between the subsequent readings, are negligible. Changes in the resistance of the voltameters during the progress of an experiment are largely responsible for the drift of the current and, therefore, the number of voltameters that can be used in any experiment is limited practically to six. Two voltameters of each laboratory were used in each experiment.

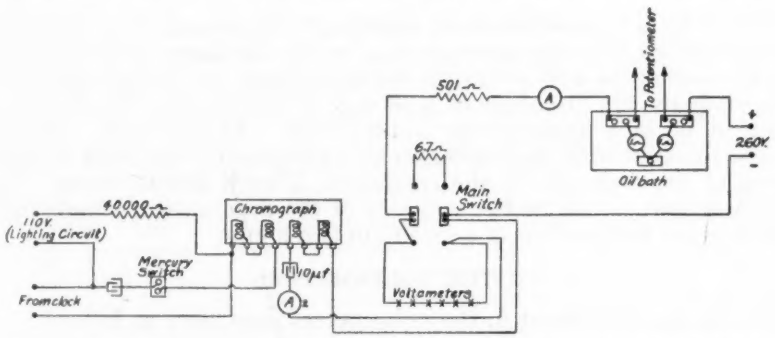

FIGURE 2.—*Voltameter circuit at the Physikalisch-Technische Reichsanstalt*

TABLE 14.—*Integrated value of potentiometer readings during the voltameter experiments*

Experiment No.	N. P. L. values	P. T. R. values	B. S. values	Experiment No.	N. P. L. values	P. T. R. values	B. S. values
1	1.012585	1.012585	1.012582	6	1.005631	1.005631	1.005632
2	1.017114	1.017113	1.017114	7	1.019019	1.019020	1.019020
3	1.018145	1.018146	1.018145	8	1.017457	1.017458	1.017458
4	1.015176	1.015177	1.015176	9	1.016711	1.016714	1.016712
5	1.015327	1.015328	1.015326	10	1.018794	1.018795	1.018796

The compensating resistance through which the current flowed prior to starting the deposit was adjusted, as nearly as possible, to the initial resistance of the voltameters. The ballast resistance was then set to give a preliminary value of current that was convenient for the potentiometer measurements. The standard resistances were two 1-ohm coils immersed in oil, the temperature of which was read periodically.

The potentiometer was provided with five dials. During the experiment no adjustment of the potentiometer current was made. Its value, however, was such that a normal cell gave a reading of about 1.0183. Periodic readings of a control cell were made during the experiment, and at the conclusion of the experiment the reading of the reference cell was taken for relating the measurements to the primary reference group. The best condition is for the readings during the experiment to involve the same coils in the potentiometer as used for measuring the control and reference cells. This is impractical, however, but the largest differences involve no dials higher than the millivolt dial.

2. MEASUREMENT OF TIME

The ticks of a standard clock, omitting 0, 15, 30 and 45 second ticks, were recorded on a chronograph tape by the discharge of a condenser. On the same tape a record of the beginning and end of the experiment was made by the discharge of a second condenser (fig. 2) which was charged initially through the voltameters. An ammeter, *A2*, was placed in series with the condenser as a safeguard to indicate a breakdown of the dielectric in the condenser, if such should occur. The Reichsanstalt estimates the accuracy of the time measurements to be within a few hundredths of a second in two hours.

3. THE VOLTAMETERS

Except in experiment 6, the voltameters used were as follows:

Laboratory	Kind of voltameter	Capacity of platinum cup
		ml
B. S.	Smith form	350
N. P. L.	do	350
P. T. R.	Kohlrausch	90

In the sixth experiment the B. S. voltameters were of the porous-cup form with small platinum cups, capacity 125 ml, and the N. P. L. voltameters were of the Smith form with small cups of 100 ml capacity.

4. PREPARATION OF PLATINUM CUPS

Three large platinum cups and three small platinum cups were available for the bureau's part in these experiments. The large cup, No. 93, is one in which no deposits of silver have ever been heated to a sufficiently high temperature to expel inclusions. Cup No. 92, however, had been subject to such treatment. As a result the inner surface of cup No. 92 has been somewhat modified from the condition in which it was used in the work of the international technical committee of 1910. It will be shown in the results that follow that no significant difference was observed in the deposits obtained in these two cups and

therefore the present work should tie in accurately with the earlier measurements so far as the condition of these platinum cups is concerned. Cup No. 94 was used as a counterpoise in weighing cups Nos. 92 and 93. Both of the smaller cups, Nos. 27 and 28, had been heated with deposits in determining the inclusions. The counterpoise for weighing the small cups was No. 39.

The platinum cups of the B. S. and N. P. L. voltameters were prepared for each experiment by first removing the previous silver deposit by electrolysis, following which they were filled with nitric acid (1 part acid to 2 parts water) and allowed to stand for about one hour. They were then washed with water, chromic acid, and several changes of distilled water. The B. S. cups were then dried by glowing them in a flame, but the N. P. L. cups were dried in an oven at 120° C. The glowing process was chosen for the B. S. cups because this had been found effective [15] in preventing absorption effects in the case of platinum cups in which silver deposits had been heated to high temperatures to expel inclusions. The P. T. R. cups were immersed in a solution of nitric acid and distilled water to dissolve out the silver of the preceding experiment following which they were washed and dried by glowing in a flame.

5. PREPARING THE ANODES

The anodes for the B. S. and N. P. L. voltameters were covered with a layer of electrolytic silver that was deposited by electrolysis during the first step in cleaning the platinum cups. This was done by passing a current of about 0.1 ampere through the voltameters in the reverse direction during the night. The silver deposited on the anode was crystalline and adherent. The anodes were washed in distilled water and glowed in a flame. After glowing the electrolytic silver presented a very brilliant appearance. The P. T. R. anodes were solid cylinders of purest silver obtained from the Deutsche Gold- und Silberscheideanstalt in Frankfurt a. M. and were used without depositing electrolytic silver upon them. Following each experiment they were washed and glowed in a flame.

6. THE ELECTROLYTE

The B. S. silver nitrate was purified by recrystallization and fusion starting with the chemically pure material of reagent grade available in the bureau's stores. The final tests on the purified product indicated that it was very close to neutral, but on the acid side by less than 1 part in 1,000,000. The permanganate test [16] for reducing impurities gave values from 6 to 20 minutes without decolorization of one-half ml of $N/1{,}000$ potassium permanganate added to a sample of about 10 g of silver nitrate in a solution of 10 ml. These tests indicate that the silver nitrate for the present investigation was equal to or better than that previously employed for the voltameter work at this bureau.

The silver nitrate used in the B. S. voltameters was a 10 per cent solution and this was freshly prepared for each experiment.

The N. P. L. electrolyte was similarly prepared and tested. As some solutions proved to be slightly basic, small quantities of nitric acid

[15] B. S. Bulletin, vol. 13, p. 157, 1915.
[16] B. S. Bulletin, vol. 9, p. 531, 1913.

were added on several occasions. The concentration of the solution for the N. P. L. voltameters was varied at will between 10 and 15 per cent. A fresh solution was prepared for each experiment.

The P. T. R. electrolyte was prepared from fused silver nitrate which was purchased from the Deutsche Gold- und Silberscheideanstalt. Before preparing the solution, however, the sticks were individually washed with distilled water. The P. T. R. solutions were 20 per cent.

For the sixth experiment the solution in all voltameters was 10 per cent B. S. silver nitrate. For all other experiments the delegates made use of their own material.

Measurements for acidity using methyl red as the indicator were made by the N. P. L. and B. S. delegates and when necessary small corrections have been made to the final values of E calculated from the silver deposits. This has been done in accordance with previous determinations [17] on the effect of small amounts of acid in decreasing the deposits. Measurements of the acidity of the P. T. R. electrolyte were also made, by permission, and it was found that the solution averaged about 4 parts in 10^6 acid which would permit a correction to the final results of 2 in 100,000 (increase). This correction has not been applied, however, in this report.

7. WASHING THE DEPOSITS

At the close of each experiment the glass traps of the Smith form voltameters used by B. S. and N. P. L. were closed and the anodes and anolytes removed. The silver nitrate remaining in the cups was then syphoned off. Following this the cups were filled with distilled water and emptied by syphon six times. The electrolyte and wash waters were examined in a strong light for loose particles of silver. When found, these were added to the respective deposits, but in most cases the electrolyte and wash waters were entirely free of loose particles of silver. After being washed, the cups containing deposits were dried in an oven for one hour or more at 120° C. When the cups were removed from the oven they were placed in desiccators to cool before weighing.

The P. T. R. voltameters were dismantled at the conclusion of the deposit by removing the anode and glass cup which contained most of the anode slime. The silver nitrate was poured out into a large beaker and the cup filled with distilled water three times. The wash waters were poured into the same beaker with the electrolyte. The platinum cups were then completely immersed in distilled water and allowed to remain so for 24 hours after which they were removed and dried in the oven at 150° C. The electrolyte and wash waters were filtered through a disk of filter paper in a gooch crucible and the paper examined for loose silver which should be added to the deposits. After drying the deposits the platinum cups were placed in desiccators before weighing them.

8. WEIGHING THE PLATINUM CUPS

In preparation for the weighings, two silver weights which are gold-plated were recalibrated and the masses certified by the bureau. Actually the weight *S2* alone was used in Berlin for weighing deposits

[17] S. B. Bulletin, vol. 10 p. 482, 1913.

of the Bureau of Standards and those of the National Physical Laboratory. This weight was restandardized at the N. P. L. following the completion of the voltameter experiments in Berlin. The values before and after the measurements are as follows:

	g
April, B. S. value	4. 09766
August, N. P. L. value	4. 097658

The agreement of the two certified values is therefore very satisfactory. To allow for small variations of a few milligrams in the deposits from the actual value of this standardized weight, a small assay set of weights was employed. This also had been standardized and certified by the bureau.

Weighings were made on a Rueprecht balance in the constant-temperature room. The balance was read by telescope and scale from a distance and was operated by rods and levers. The platinum cups were counterpoised by similar platinum cups and the silver was balanced by the small silver weight mentioned previously. To this was added or subtracted the few milligram weights of the assay set that were necessary to effect a balance. The N. P. L. followed a similar procedure. The P. T. R. cups were weighed against a solid platinum weight and the silver against other weights to which a correction for the buoyancy of the air was applied.

Differences between the cups, deposits, and counterpoises were computed from the swings of the balance. The B. S. and N. P. L. cups were weighed singly against the respective counterpoises and then against each other. The weighings checked in all cases to a few hundredths of a milligram and small residual errors were treated by the method of least squares.

TABLE 15.—*Silver deposits*

[Experiment No. 6 B. S. used cups 27 and 28; N. P. L. used cups 4 and 5]

Experiment	B. S. voltameters		N. P. L. voltameters		P. T. R. voltameters			
	93	92	1	3	1	2	3	4
	mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
1	4, 091. 89	4, 091. 72	4, 091. 88	4, 091. 65	4, 092. 37	4, 092. 61		
2	4, 093. 28	4, 093. 17	4, 093. 47	4, 093. 46			4, 092. 90	4, 092. 82
3	4, 096. 00	4, 095. 91	(4, 096. 50)	(4, 096. 83)	4, 095. 97	4, 095. 77		
4	4, 085. 56	4, 085. 43	4, 085. 35	4, 085. 38			4, 085. 10	4, 085. 40
5	4, 086. 15	4, 086. 21	4, 085. 98	4, 086. 12	4, 086. 23	4, 086. 11		
6	4, 080. 74	4, 080. 59	4, 081. 44	4, 081. 38			4, 080. 16	4, 080. 17
7	4, 101. 20	4, 101. 23	4, 101. 16	4, 101. 22	4, 101. 57	4, 101. 75		
8	4, 094. 95	4, 095. 07	4, 094. 95	4, 094. 83			4, 094. 66	4, 094. 53
9	4, 091. 05	4, 091. 10	4, 091. 16	4, 091. 27	4, 091. 50	4, 091. 18		
10	4, 168. 14	4, 168. 24	4, 168. 15	4, 168. 11			4, 168. 16	4, 168. 10
Sum	40, 988. 96	40, 988. 67	40, 990. 04	40, 990. 25	20, 467. 64	20, 467. 42	20, 520. 98	20, 521. 02
Total	81, 977. 63		81, 980. 29		81, 977. 06			

NOTE.—Maximum difference of total deposits 4 in 100,000.

9. THE SILVER DEPOSITS

Table 15 records the silver deposits and shows how reproducible the voltameter deposits are assuming there is no error from any other source.

The two B. S. voltameters agreed to within 0.3 mg of silver in a total for the 10 deposits of 41 g of silver in each cup. The total deposits in the B. S. and P. T. R. voltameters agreed to within 0.6 mg in 82 g of silver. It has been necessary to include in the addition several determinations (bracketed values in table) which were rejected in computing the final results, but notwithstanding this, the agreement of the sum totals of the weights of deposits in voltameters of the three countries is good.

10. FINAL RESULTS WITH THE VOLTAMETERS

The final results for the electromotive force of the P. T. R. Kleiner Stamm using the P. T. R. "international ohm" are given in Table 16. The values from one experiment to the next seem to scatter more than would be expected from the concordance of the silver deposits listed in Table 15. These final values involve the errors in measuring the current and time as well as the errors in the voltameters themselves. It appears that the errors in measuring current and time are greater than in the manipulation of the voltameter.

TABLE 16.—*Silver voltameter results at the Physikalisch-Technische Reichsanstalt*

[Measurement of the emf. of the Kleiner Stamm in terms of the silver deposits and the P. T. R. international ohm]

Date	B. S. voltameters			N. P. L. voltameters			P. T. R. voltameters		
	Emf	Δ	Weight	Emf	Δ	Weight	Emf	Δ	Weight
1931									
June 5	1.01812	−8	2	1.01811	−10	2	1.01828	+9	2
June 10	30	+10	10	36	+15	10	21	+2	10
June 15	23	+3	10	(basic) [40]			21	+2	10
June 18	23	+3	10	20	−1	10	17	−2	10
June 24	22	+2	10	18	−3	10	21	+2	10
June 26	15	−5	2	33	+12	2	03	−16	2
June 29	24	+4	10	23	+2	10	35	+16	10
July 2	26	+6	10	24	+3	10	17	−2	10
July 6	07	−13	10	11	−10	10	13	−6	10
July 9	15	−5	10	13	−8	10	13	−6	10
Mean	1.01820			1.01821			1.01819		
Probable error of single observation	4			5			5		
Weighted mean	1.01820			1.01820			1.01819		

Summary

B. S. voltameters	1.01820
N. P. L. voltameters	1.01820
P. T. R. voltameters	1.01819
Mean of all	1.01820
Probable error	1

The mean results of 10 experiments show a very satisfactory agreement between the B. S., N. P. L., and P. T. R. voltameters. The mean of all is 1.01820 with a probable error of 1 part in 100,000.

At the close of the work, a conference was held at which the following were present: Prof. Dr. Giebe, chairman; Prof. Dr. Jaeger; Prof. Dr. von Steinwehr; Mr. Vigoureux; and Mr. Vinal.

It was agreed that—

1. The present work supports the conclusions of the International Technical Committee of 20 years ago in establishing the electromotive force of the Weston normal cell as 1.0183 volts at 20° in terms of international units.

2. The present comparison of standard cells and the voltameter results are concordant in indicating that the P. T. R. unit for the volt at the time of these measurements was too low by about 1 in 10,000.

VI. DISCUSSION OF THE DIFFERENCES IN THE UNITS

When the silver voltameter is used to determine the value to be assigned to a group of standard cells or to verify a value previously determined, it is necessary to employ also standards of resistance for which values are known in terms of some specified unit. The differences which may be observed from time to time in the value of electromotive force of a group of cells by voltameter measurements include, therefore, changes in the unit for the ohm as well as changes in the electromotive force of the cells. The value determined in the course of this work for the electromotive force of the Kleiner Stamm at the Reichsanstalt is based on the P. T. R. standard for the international ohm and the mean result of the voltameter measurements by representatives of the three laboratories. The concordance of the voltameter measurements indicates that the international ampere as defined by the silver deposits of the three laboratories is the same to within 1 part in 100,000.

Direct comparisons of standards of electromotive force and resistance have revealed much larger differences to exist between the various laboratories. The voltameter measurements by the three laboratories jointly in Berlin fulfill the recommendation [18] of the Advisory Committee on Electricity to the International Committee on Weights and Measures.

In the course of ordinary electrical measurements, the international ampere is based on measurements of electromotive force (E) and resistance (R) and not on the "silver ampere" of the voltameter, although that is the fundamental unit. In Figure 1 are given diagrammatically the differences in millionths which have been found for the ampere based on measurements of E and R at the several laboratories. These differences are greater than for either E or R singly because both are involved.

The watt which is derived from measurements of E and R in the course of ordinary work involves the differences in R and twice the differences in E as may be seen by writing the formula

$$W=\frac{E^2}{R}$$

It is not surprising, therefore, that the differences in the watt as measured at the several laboratories are greater than for the other units. The maximum difference is 198 millionths as shown in Figure 1.

Since direct comparisons of the ohm and volt standards were made, it is possible to translate the voltameter results into the approximate

[18] Report, Comité Consultatif d'Électricité, p. 23, 1930.

values which would have been obtained at Paris, Teddington, or Washington, if the voltameter measurements had been made in those places, employing the reference groups of cells and resistance standards of the respective laboratories. The results are as follows:

TABLE 17.—*Observed and calculated values of the standards of electromotive force at the four laboratories*

Place	Units	Emf at 20° C.	Remarks
Berlin	P. T. R.	1.01820	Observed.
Paris	L. C. E.	1.01817	Calculated.
Teddington	N. P. L.	1.01830	Do.
Washington	B. S.	1.01827	Do.

The inference drawn from these results is that the unit of the N. P. L. corresponds exactly to the value defined for the Weston normal cell at 20° C. by the International Technical Committee of 20 years ago. The units for the other laboratories are slightly lower. The value for Washington in terms of B. S. units is, however, exactly the same as the result of the bureau's own experiments on the voltameter [19] published in 1913. The value observed in Berlin in P. T. R. units is less than the electromotive force determined [20] for the Kleiner Stamm when voltameter measurements were last made there by approximately 1 in 10,000. No previous figures on the L. C. E. standard are available for comparison.

VII. CONCLUSIONS

1. The comparisons which have been made between the standards for the international electrical units of four national laboratories have shown significant differences to exist, although a uniform basis for the international units was provided by the agreement among the laboratories, effective January 1, 1911.

2. The maximum difference for the international ohm, as the unit is maintained at these laboratories, is 74 millionths. Two laboratories have recently corrected their measurements by about 3 in 100,000 as a result of their latest mercury-ohm determinations. These corrections, however, fall within the maximum limits of the difference mentioned above.

3. The standards for the volt, which are groups of Weston normal cells, differ in electromotive force by as much as 1 part in 10,000. A highly concordant series of voltameter experiments has now been made which confirms the recommendation of the International Technical Committee in defining the electromotive force of the Weston normal cell as 1.0183 international volts at 20° C. These same voltameter measurements indicate that the groups of cells having the lower values at the present time are appreciably below the normal value.

4. The international ampere as determined by the silver deposits of three of the national laboratories is the same to within 1 part in 100,000. The agreement on this fundamental unit indicates that a

[19] B. S. Bulletin, vol. 10, p. 490, 1913.
[20] Zeit. f. Instrk., vol. 42, p. 221, 1922.

readjustment in the electromotive force assigned to certain groups of cells may safely be made.

5. At the present time, the international ampere used in ordinary measurements is based on working standards of electromotive force and resistance. These differ as mentioned above and, therefore, the working representation of the international ampere of the several laboratories based on E and R, differs by as much as 136 millionths. This difference could be much reduced by a readjustment of values assigned to the working standards of electromotive force and resistance.

6. The unit of power, the watt, is usually measured in terms of E and R and, therefore, involves twice the differences that have been found in standards for the former and also the differences in standards for the latter. The maximum spread in the unit for the watt between the several laboratories is 198 millionths.

7. The results of the present work indicate that a readjustment of the values assigned to standards for the ohm and volt is needed. Such a step is not to be taken ill-advisedly, however, but after agreement of properly constituted authorities. The question involved has broader aspects than a mere readjustment of values assigned to standards on the basis of the international units. Other investigations on the absolute measurement of the ohm and the ampere, the discussion of which is outside of the scope of this paper, have shown that the international standards for the ohm and, consequently, the volt also do not represent the absolute units of resistance and electromotive force as closely as was believed 20 years ago. The Advisory Committee on Electricity to the International Committee on Weights and Measures has expressed its opinion in the first report dated February 11, 1929, that the absolute system of electrical units based on the cgs system ought to replace the present international system for all scientific and industrial determinations.

If this is to be done, the change in the units for the ohm and the volt will amount to 5 parts in 10,000, which is much larger than the present discrepancies between the international standards. Rather than make two adjustments of the electrical standards in the next few years, the present discrepancies seem an added argument for passing quickly to the absolute basis for the units by a single adjustment of values. Such a step would unify the systems of mechanical, thermal, and electrical measurements on a sound theoretical basis, but would not lessen the vigilance required of the national laboratories to preserve the constancy and equality of the working standards. There seems little doubt that the working standards of the future, as in the past, will be wire standards of resistance and the Weston normal cell. The results of the present work emphasize the necessity for close cooperation between the national laboratories in order that correct and uniform electrical standards may be maintained.

WASHINGTON, March 16, 1932.

A METHOD FOR THE PURIFICATION OF RUBBER [1] AND PROPERTIES OF THE PURIFIED RUBBER

By A. T. McPherson

ABSTRACT

Purified rubber was prepared by the digestion of crude rubber or latex with water at about 190° C., followed by extraction with water and with alcohol, and drying in an atmosphere of inert gas. The digestion hydrolyzed the proteins, and the extraction removed the hydrolysis products, resins, and other impurities. The purified rubber contained about 99.5 per cent of rubber hydrocarbon. Properties of the rubber hydrocarbon at 25° C. were: Density, 0.9060; refractive index, 1.5184; dielectric constant at 1,000 cycles per second, 2.37; power factor at 1,000 cycles per second, 0.0015; conductivity at the end of 1 minute, 2.2×10^{-7} mho. The electrical properties measured on 14 samples were apparently independent of the botanical source or the kind of crude rubber.

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I. INTRODUCTION

This paper describes a simple procedure which was used to purify rubber for a study of the electrical properties of the system, rubber sulphur. The method of purification was one in which the non-hydrocarbon constituents of the raw rubber were removed by extraction, the proteins being first hydrolyzed by digestion with water at an elevated temperature. The solvents with which the rubber was extracted were water and alcohol. These removed the protein disintegration products, sugars, fatty acids, and other resinous and minor constituents, and yielded a product which was about 99.5

[1] The preparation of rubber hydrocarbon of high purity by the crystallization and distillation of rubber is the subject of a research being conducted by other investigators at this bureau. See Technical News Bulletin of the Bureau of Standards No. 161, p. 85; September, 1930. Also, E. W. Washburn, Crystalline Rubber Hydrocarbon, Phys. Rev., vol. 38, pp. 1790–91; 1931.

per cent rubber hydrocarbon. While this method of purification involves no distinctly original features it is here given in some detail, since it may be of interest to other investigators who may wish to prepare for experimental purposes large quantities of rubber hydrocarbon of reasonable purity without an excessive expenditure of time.[2]

The dielectric constant, power factor, and conductivity of purified rubber prepared from different kinds of crude rubber were relatively consistent, and showed no variations which might be attributed to the botanical source or kind of rubber.

II. DESCRIPTION OF THE PURIFICATION PROCESS

Various procedures were tried for the purification of rubber from latex or crude rubber. The procedure which proved the simplest and most generally satisfactory consisted in digestion with water, extraction with water and with alcohol, and drying in an inert gas.

1. DIGESTION WITH WATER

Crude rubber or latex was digested with water at an elevated temperature in an autoclave. The crude rubber, in lots of several kilograms, was sheeted thin and put into a Pyrex glass cylinder with sufficient water to cover it. The cylinder was placed in the autoclave in such a way that the rubber was not exposed to contamination by iron or copper salts from the autoclave or its fittings. Since the autoclave was heated by means of steam circulated through a jacket a quantity of water was placed in the bottom of the autoclave to facilitate heat transfer to the pyrex jar and its contents. Ammonia-preserved latex, when used instead of crude rubber, was placed in the pyrex cylinder with no previous treatment other than straining. The autoclave was heated to about 190° C., which is the temperature of steam at a pressure of 167 pounds per square inch in excess of atmospheric pressure. The time of digestion was ordinarily three to four hours, exclusive of the time required for heating and cooling the heavy autoclave. The time and temperature of heating were probably in excess of that necessary to hydrolyze the proteins, but were employed in order to insure thorough penetration of the crude rubber by the water.

At the conclusion of the digestion the water in which the rubber had been heated was dark colored and contained considerable organic matter. When latex was employed it was always found coagulated after digestion. A hand examination of the digested rubber indicated that the digestion process did not soften or degrade the rubber to any great extent.

2. WASHING WITH WATER AND ALCOHOL

The digested rubber was washed and extracted in order to remove protein disintegration products, resins, sugars, soluble inorganic salts, and possible mechanical impurities. The washing and extraction were carried out with the use of an internal mixer of a type which was designed for the compounding of rubber.[3] The mixing chamber

[2] This method is similar to the one described by Kemp, J. Franklin Inst., vol. 211, pp. 44–47; January, 1931. The work here reported was done prior to the publication by Kemp. See Technical News Bulletin of the Bureau of Standards, No. 128, pp. 2–3; December, 1927.

[3] This internal mixer is described in Technical News Bulletin of the Bureau of Standards, No. 141, pp. 1–2; January, 1929, and also in India Rubber World, vol. 80, No. 1, p. 78, April, 1929.

was provided with a cover fitted with a reflux condenser to prevent the loss of solvent. The mastication of the rubber with the solvent in the internal mixer was a much more effective means of removing these various impurities than was percolation of the thinly sheeted material with the solvent in an extraction apparatus. The chief advantage of the internal mixer lay in the constant renewal of the surface of the rubber. This facilitated the removal of any mechanical impurities and pockets of solution, and probably accelerated greatly the extraction of substances slightly soluble in rubber. Furthermore, the use of the internal mixer obviated various difficulties which are attendant on the extraction of soft rubber in lots of several kilograms in an apparatus of the Soxhlet type.

The process of washing and extracting the digested rubber with water usually occupied 4 hours, during which time the water was changed every 15 or 30 minutes. Distilled water was used, and was kept vigorously boiling in order to exclude air and thus prevent oxidation of the rubber. At the end of the period the wash water was practically colorless and left only a very slight residue on evaporation.

Treatment with water was followed by a similar treatment with alcohol. For this purpose ethanol, containing not over 5 per cent of water and 10 per cent of methanol, was used. Alcohol was employed as a solvent for extracting the resinous constituents of rubber rather than acetone on account of its higher boiling point. When rubber was extracted with acetone at its boiling point, 56° C., a soft and almost pasty product was obtained on account of the mechanical working of the rubber at the relatively low temperature.

Extraction with alcohol was followed by a few minutes extraction with one or two portions of boiling water in order to remove the alcohol. This was done because, in the subsequent drying, it seemed easier to remove the water than the alcohol. This point, however, was not investigated critically.

3. DRYING

The extracted rubber was dried by working it in the internal mixer at a temperature of 110° to 125° C. in an atmosphere of inert gas, usually nitrogen. A continuous stream of gas was passed through the mixer during the drying, which was ordinarily continued for about 30 minutes after steam had disappeared from the effluent gas.

III. COMPOSITION OF THE PURIFIED RUBBER

No extensive study was made of the composition of the purified rubber. Determinations of nitrogen, benzene-insoluble constituents, and ash were made on representative preparations. Combustion analyses of high precision were made on two samples of the purified rubber.

1. NITROGEN

Nitrogen was determined by the Kjeldahl method, using 2 g samples of rubber. The results of analyses on rubber before and after purification are given in Table 1. The nitrogen content of the original unpurified rubber was 0.3 to 0.6 per cent, while that of seven lots of the purified material ranged from 0.02 to 0.05 per cent, with an average value of about 0.03 per cent. The precision of the determination was of the order of 0.01 per cent.

2. ASH

Determinations of ash were made by igniting 5 g samples of rubber in crucibles of approximately 100 ml capacity in an electrically heated muffle furnace, observing the usual precautions. In most cases an appreciable reduction in ash content resulted from purification. Only in the case of a sample of Guayule rubber was there a small increase in percentage of ash. This may have resulted from the removal of a larger proportion of resins than of inorganic material in the purification process. The ash content of purified rubber made from clean plantation rubber or latex ranged from 0.04 to 0.24 per cent, with an average of about 0.12 per cent. Analyses made by ignition in a muffle and in a combustion furnace were in good agreement. Seven determinations on one preparation, by the former method, indicated an ash content of 0.15 ± 0.02 per cent, while five determinations by the latter method, which are reported in Table 2, gave the result 0.13 ± 0.03 per cent.

3. BENZENE-INSOLUBLE CONSTITUENTS

The benzene-insoluble fraction of rubber was determined by dissolving 5 g samples in 50 to 100 ml of benzene to which about 1 g of trichloroacetic acid had been added. On exposure to light for a few hours a limpid solution was obtained from which proteins, salts, and foreign materials, such as dirt or bark, could easily be separated by centrifuging. The residue was thoroughly washed with benzene and dried before it was weighed. The results which are given in Table 1 indicate that the original unpurified rubber contained from 2.5 to 5 per cent of insoluble material, and the purified rubber 0.1 to 0.3 per cent.

TABLE 1.—*Composition of rubber before and after purification*

Source of rubber	Preparation No.	Nitrogen		Benzene-insoluble		Ash	
		Before purification	After purification	Before purification	After purification	Before purification	After purification
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Smoked sheet	3	0.29	0.02	2.50	0.18	0.18	0.08
Guayule [1]		.30	.05	8.1		1.03	1.27
Pale crêpe	6	.31	.02			.16	.14
	7		.03				
	8		.03				
	10		.02				.07
Latex-sprayed rubber	4	.62	.02	5.35	.26	1.4	.24
Hevea latex	11		.02				.04
	14						.15
	[2] 19		.004		.33		.19
	[3] 23				.13		.08
	[3] 27				.31		

[1] The Guayule rubber was digested with 4 per cent potassium hydroxide solution instead of water to destroy woody matter.

[2] This sample of purified rubber was prepared by A. D. Cummings using the method of Cummings and Sebrell, Ind. Eng. Chem. vol. 21, p. 553, June 1929.

[3] These samples were prepared and analyzed by A. D. Cummings.

4. CARBON, HYDROGEN, AND OXYGEN

Organic combustion analyses on three preparations of purified rubber were made with an apparatus capable of giving results of relatively high accuracy.[4] The results are shown in Table 2. The sums of the carbon, hydrogen, and ash found in the different analyses ranged from 99.82 to 100.06 per cent, with an average value of 99.95 per cent. Assuming the nitrogen content to be 0.03 per cent, the oxygen indicated by difference is only 0.02 per cent. This is evidence that practically all the resins and other nonhydrocarbon constituents were removed by the extraction process, and that the rubber did not suffer appreciable oxidation in the process of purification.

The above data do not warrant an exact statement of the purity of the rubber. If it is assumed, however, that the chief impurities are inorganic substances, proteins, or their degradation products and moisture, the sum of these is probably not in excess of 0.5 per cent, or the hydrocarbon content of the rubber may be estimated at about 99.5 per cent.

TABLE 2.—*Combustion analyses on purified rubber*

Source of rubber	Analysis No.	Carbon	Hydrogen	Ash	Total
		Per cent	*Per cent*	*Per cent*	*Per cent*
Pale crêpe	1	87.87	11.76	0.19	99.82
	2	87.75	11.95	.25	99.95
Hevea latex	1	87.99	11.89	.18	100.06
	2	88.05	11.87	.10	100.02
	3	87.95	11.87	.10	99.92
	4	87.94	11.85	.15	99.94
	5	88.01	11.86	.10	99.96
Calculated for C_5H_8		88.15	11.85		100.00

IV. PROPERTIES OF THE PURIFIED RUBBER

The purified rubber was dark in color, except when viewed in thin layers. The colored constituents were probably present in small amount and originated during the digestion with water at the high temperature.

No measurements were made of the consistency of the purified rubber. By hand examination it seemed to be comparable to or somewhat softer than crude rubber which had been thoroughly masticated or "broken down." The consistency was probably the result of the mechanical working accorded the rubber during the extraction and drying.

Determinations of the density and the refractive index were made on single samples of the purified rubber which had been prepared from latex. Dielectric constant, power factor, and conductivity measurements were made on all samples of the purified rubber.

[4] These analyses were made by H. J. Wing using the method described by Washburn, Bruun, and Hicks, B. S. Jour. Research, vol. 2 (RP45), p. 487, March, 1929.

1. DENSITY

The density of the purified rubber was determined at three temperatures with the use of a Pyrex glass pyknometer in which mercury was employed as the confining liquid.[5] The density at 0° C. was 0.9209; at 20°, 0.9088; and at 61.2°, 0.8845. These values, when plotted against the temperature, lie on a straight line within probable experimental error, as is indicated by Figure 1. The density at 25°, taken from the curve in this figure, is 0.9060. The coefficient of change in density with temperature is 0.000595 per degree, between 0° and 61.2°, or the density at any temperature, t, in this range is given by the relation,

$$d_t = 0.9060 + 0.000595\ (25 - t)$$

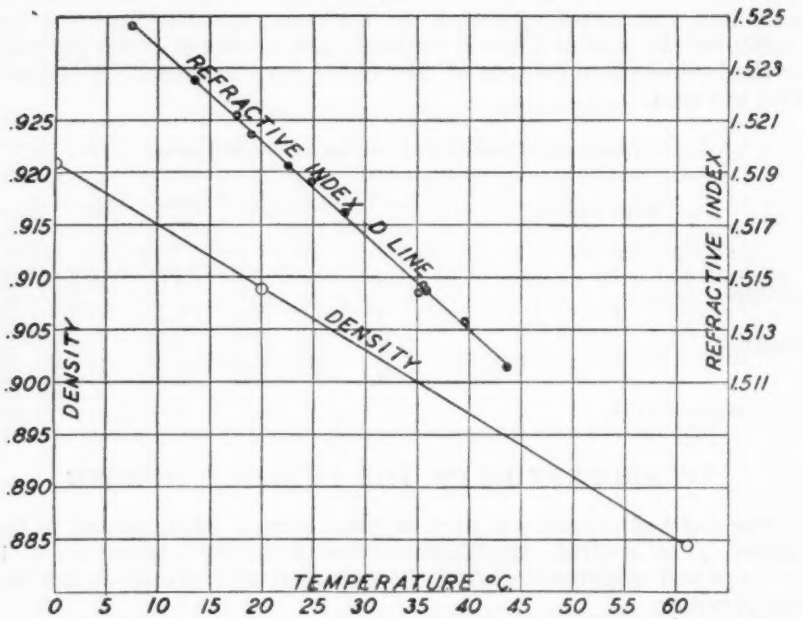

FIGURE 1.—*Density and refractive index of purified rubber*

By way of comparison the density of standard grades of commercial crude rubber at 25° C. is about 0.912, and the change in density per °C. is 0.00062.[6]

2. REFRACTIVE INDEX

The refractive index of the purified rubber for the D line of sodium was measured with an Abbé prism refractometer. Thin specimens suitable for measurement in this instrument were prepared by pressing out small sheets of rubber between layers of aluminum foil. These were applied to the prism and pressed against it so as to make optical contact without the use of a liquid. The temperature at which the determinations were made was controlled by circulating water around

[5] The density determinations were made by A. D. Cummings.
[6] A. T. McPherson, Density of Rubber-Sulphur Compounds, B. S. Sci. Paper, No. 560, 1927.

the prisms. The results which were obtained at temperatures from 7° to 43° C. are shown graphically in Figure 1.

The refractive index of the purified rubber for the *D* line at 25° C., taken from the curve in Figure 1, is 1.5184, which is approximately the same as the value 1.519 reported previously for crude rubber.[7] The refractive index at temperatures other than 25° C. is given by the relation

$$n^t{}_D = 1.5184 + 0.00036\ (25 - t)$$

The experimental results agree with the values indicated by this equation with a maximum deviation of 0.0004 and an average deviation of 0.0001.

3. ELECTRICAL PROPERTIES

Dielectric constant, power factor, and conductivity measurements were made on samples of purified rubber which had been prepared not only from wild and plantation Hevea rubber, but also from other natural rubbers of widely different botanical sources. The method of preparing test specimens and making electrical measurements is described fully elsewhere.[8] The results of these measurements are summarized in Table 3.[9]

The dielectric constant at 1,000 cycles per second and 25° C. of all the samples of purified rubber which were examined was between 2.33 and 2.40, with an average value of 2.37. The dielectric constant of the unpurified rubber is higher and more variable than this, ranging from 2.50 to 2.70 in most cases. The value, 2.37, probably approximates the dielectric constant of pure rubber hydrocarbon.

The power factor of purified rubber measured at 1,000 cycles per second was less than that of rubber before purification, and ranged from 0.0008 to 0.0026, with an average value of 0.0015. This variability, in the light of general knowledge of power factor, may be attributed to residual impurities in the rubber, including moisture. The true power factor of rubber hydrocarbon is probably less than 0.0008, the lowest value found, because traces of most impurities are known to increase the power factor of hydrocarbons above the true value.

The conductivity of purified rubber, measured one minute after the application of potential, was decidedly lower and less variable than that of crude rubber. For different samples the conductivity ranged from 1.4 to 3.6×10^{-17} mho, with an average of 2.2×10^{-17} mho. As in case of the power factor the average conductivity is not to be regarded as the true conductivity of a hydrocarbon, since the effect of impurities is always to increase, never to decrease, the conductivity of the main constituent. Consequently, the conductivity of pure rubber hydrocarbon is in all probability smaller than the lowest value here reported.

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[7] H. L. Curtis and A. T. McPherson, Dielectric Constant, Power Factor, and Resistivity of Rubber and Gutta-Percha, B. S. Tech. Paper No. 299, p. 698, 1925. See also Cecil W. Shacklock, Further Studies of Rubber Solutions, Inst. Rubber Ind., Trans. vol. 7, p. 356; 1932.

[8] H. L. Curtis, A. H. Scott, and A. T. McPherson, Properties of the System, Rubber Sulphur. Part III. Effect of Temperature and Frequency on the Dielectric Constant, Power Factor, and Conductivity. In preparation.

[9] The electrical measurements were made by A. H. Scott.

TABLE 3.—*Electrical properties of purified rubber at 25° C.*

Kind of crude rubber or latex	Botanical source	Preparation No.	Dielectric constant [1]	Power factor [1]	Conductivity [2]
					Mho×10^{17}
Penang	*Ficus elastica*		2.39	0.0018	2.7
Guayule [3]	*Parthenium argentatum*		2.33	.0011	3.7
Gaboon ball	Probably *Landolphia*		2.40	.0013	3.3
Fine Para	*Hevea brasiliensis*	2	2.37	.0008	1.6
Smoked sheet	do	3	2.36	.0008	1.6
Latex-sprayed	do	4	2.35	.0014	2.2
Pale crêpe	do	1	2.39	.0010	1.7
	do	6	2.36	.0017	1.5
	do	8	2.37	.0016	1.9
Ammonia-preserved latex	do	0	2.39	.0018	2.2
	do	11	2.36	.0018	2.0
	do	14	2.37	.0014	2.6
	do	27	2.39	.0026	
	do	31	2.41	.0022	1.7
Average for all samples			2.37	.0015	2.2

[1] The dielectric constant and power factor were measured at a frequency of 1,000 cycles per second.
[2] The conductivity was measured one minute after the application of potential.
[3] The purification of the guayule rubber used for these measurements included solution in benzene, filtration, and precipitation with acetone to effect the removal of woody impurities.

4. VULCANIZATION CHARACTERISTICS

No critical study was made of the vulcanization of purified rubber. Numerous samples, however, compounded with sulphur in proportions from 2 to 32 per cent by weight, exhibited a behavior on vulcanization that was apparently the same as that of similar mixtures of crude rubber and sulphur. When the samples were vulcanized from 20 to 40 hours at 140° C., the residual, uncombined sulphur was less than 0.1 per cent in all cases except those where the total sulphur was 28 to 32 per cent. In the latter cases residual sulphur was present in varying amounts up to 0.8 per cent.

WASHINGTON, April 16, 1932.

RP450

TESTS OF A BALANCED THERMOCOUPLE AND FILTER RADIOMETER AS A STANDARD ULTRA-VIOLET DOSAGE INTENSITY METER

By W. W. Coblentz, R. Stair, and J. M. Hogue

ABSTRACT

Data are given on the accuracy of the balanced thermocouple and filter radiometer as a standard ultra-violet dosage intensity meter.

The erythema produced by the radiometrically measured amount of heterogeneous ultra-violet radiation is compared with that produced by a measured amount of homogeneous radiation of the emission line of mercury, at 297 mμ, which is used as a standard.

This requires the determination of the ultra-violet spectral energy curve, and the total ultra-violet of wave lengths less than and including 313 mμ, of the source under test. An exact knowledge of the spectral erythemic response of the skin is also required (RP433).

Sources differing markedly in ultra-violet spectral energy distribution were investigated, including as extremes the sun, and the so-called "cold quartz" mercury vapor lamp.

A close agreement was found between the physiologically and the radiometrically determined erythemogenic efficiency of all the sources examined, including the sun, the Mazda S–1 and S–2 lamps, the high temperature quartz mercury arc lamp, and the carbon arcs of "therapeutic B, C, and white flame," carbon electrodes.

A specification is given (*a*) of minimum intensity to insure effective therapeutic results, and (*b*) of the erythemogenic unit of dosage; both in terms of the emission line of mercury, at 297 mμ, as a standard.

On the basis that a minimum intensity of 20 μ W/cm^2 of homogeneous radiation of wave length 297 mμ is desirable, the erythemogenic equivalent of heterogeneous ultra-violet radiation of wave lengths less than and including 313 mμ, in microwatts per square centimeter, is approximately as follows: The sun, 91; the Mazda S–1 lamp, 80; the Mazda S–2 lamp, 93; the high temperature quartz mercury arc, 58; the so-called "cold quartz" mercury vapor lamp, 36; and the therapeutic carbon arcs, 45 to 90 μ W/cm^2.

For an erythemogenic unit of dosage, 10,000 ergs/cm^2 of homogeneous radiation of the emission line of mercury at 297 mμ (2,967 A) is suggested.

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I. INTRODUCTION

During the past few years investigations have been in progress in this country and abroad, of various proposed methods of measuring the intensity, or so-called dosage of ultra-violet radiation of wave lengths less than about 315 mμ, which rays are found useful for therapeutic purposes, particularly in the healing of rickets.

These various methods are photo-electric, photochemical, photographic, and photometric. They are simple to operate; but the chief difficulty in their use is that they must be calibrated on an arbitrary basis, and there is no unchangeable source of ultra-violet radiation which can be used as a standard of comparison. This is exemplified in a recent investigation (1) [1] during the culmination of which work, certain inconsistencies were found in the photo-electric measurements, which indicated a decrease in the intensity of the source (a quartz mercury arc lamp) used as a standard.

In the preliminary search for a primary standard dosage intensity meter, the writers have tried the isolation of the ultra-violet of wave lengths less than and including 313 mμ in one wide band by means of a quartz spectrograph (4) supplemented by a barium flint glass filter, to correct for spectral impurities and scattered radiation of wave lengths longer than 313 mμ. This appeared to be the simplest means available for calibrating the photo-electric cell in absolute measure by comparison with a surface thermopile. However, in attempting to measure the ultra-violet in solar radiation, difficulties were experienced in maintaining the spectrum calibration and in isolating the ultra-violet at exactly 313 mμ, especially when using the spectropyrheliometer mounted upon a polar axis. Hence, this method of attack was discontinued, although it appeared sound in principle.

The purpose of the present communication is to show the reliability of the balanced thermocouple and filter radiometer as a dosage intensity meter, for measuring the ultra-violet radiation emitted by sources differing widely in spectral energy distribution, such as, for example, the so-called "cold quartz" mercury vapor arc in which over 95 per cent of the total radiation of wave lengths less than and including 313 mμ is contained in the resonance emission line of mercury at

[1] Figures in parentheses here and throughout the text indicate references given in the bibliography at the end of this paper.

254 mμ, and the sun which contains practically no radiation of wave lengths less than 290 mμ.

The estimation of the reliability of this device as a dosage meter is based upon a determination of the (observed and calculated) total energy required to produce a minimum perceptible erythema when exposure is made to measured amounts of heterogeneous radiation from different sources (evaluated by means of the balanced thermocouple and filter radiometer) as compared with the energy required to produce a minimum perceptible erythema on exposure of the same part of the body to a measured amount of homogeneous radiation of wave length 297 mμ, which is used as a standard.

The erythema test was selected because this method is in common use as a guide in ultra-violet radiation therapy. Furthermore, in view of the wide variation in erythemic susceptibility of pigmented and unpigmented skin, and in view of the fact that exposure to ultra-violet radiation can not be continued safely beyond the tolerance of the skin, which is indicated by the erythema produced, it is highly probable that this physiological effect will always have to be taken into consideration.

It is to be emphasized that the present measurements pertain to the amount of ultra-violet radiation that can be safely applied to the skin without producing an excessive erythema. No attempt is made to determine whether any photochemical or healing effects may be produced.

It is to be noted that while the erythemogenic efficiency of some of these sources appears to be lower, the photochemical activation (for example, ergosterol) may, perhaps, be found higher than that of other sources of higher erythemogenic value. In other words, while the herein-recorded erythemogenic efficiency data serve as a useful guide in estimating the dosage applicable without producing an excessive erythema, they do not necessarily serve as a guide in activating oils, foods, etc., and for healing purposes. This is especially true of ultra-violet radiation of wave lengths in the region of 250 mμ, which rays, according to several experimenters (6), are found to deactivate vitamin D, and, hence, should not be used for producing this particular photochemical reaction.

II. EXPERIMENTAL PROCEDURE

Preliminary to the description of the experimental details, it is relevant to recall that the long wave length limit, used in making the calculations and comparisons, is taken at 313 mμ (*a*) because erythemal and antirachitic activity practically ceases at this wave length and (*b*) because the emission line of mercury at 313 mμ is easily obtainable for radiometric measurements and as a limiting wave length in the mechanical isolation and integration of ultra-violet radiation of wave lengths less than and including 313 mμ.

Similarly the emission line of mercury at 297 mμ is taken as a standard for erythemal and radiometric comparisons (*a*) because it is close to the maximum of erythemic susceptibility, and (*b*) because it is easily obtained as a source that is readily evaluated in absolute units by direct comparison with a standard of radiation of established constancy. In these comparisons the exit slit acts as the source and no consideration of absorption in the spectroradiometer or change in intensity with aging of the lamp is necessary.

In order to obtain an accurate comparison between the physiological (erythemal) and the radiometric determinations of the ultra-violet intensity of a given source, it is necessary to obtain four important sets of data.

1. DETERMINATION OF THE ULTRA-VIOLET SPECTRAL ENERGY DISTRIBUTION OF THE HETEROGENEOUS SOURCE

The ultra-violet spectral energy distribution of the artificial sources was determined by means of a spectroradiometer, consisting of two uncemented quartz-fluorite achromatic lenses, 33 mm in diameter and 30 cm focal length, and a 60° quartz prism, 6 cm in height. The radiometer consisted of a vacuum thermopile and an iron-clad Thomson galvanometer.

The reduction of the data from the prismatic to the normal spectrum (the slit width correction), and the corrections for absorption by the fluorite window and the spectrometer, are described on page 738 of the preceding paper (3); and they are indicated in Table 1. In view of the fact that only relative and not absolute values of spectral intensities are required, the reduction of the data is somewhat simpler than in the preceding paper.

TABLE 1.—*Relative ultra-violet spectral intensities of a white flame carbon arc reduced to normal spectrum*

Observed wave length	Galvanometer deflection	Spectrometer transmission	Slit width correction	Fluorite window, transmis-	Relative energy $\frac{2}{3\times4\times5}$
1	2	3	4	5	6
mμ			mμ		
440	13.90	0.383	17.0	0.900	237
420	13.17	.386	15.6	.900	243
403	12.30	.391	14.4	.900	243
390	11.90	.394	13.2	.900	255
378	7.10	.396	12.0	.900	166
366	4.35	.398	11.0	.900	111
355	2.80	.397	10.0	.897	78.6
345	1.80	.389	9.1	.892	57.0
337	1.80	.380	8.3	.890	64.1
329	1.50	.370	7.6	.888	59.7
322	1.27	.360	7.1	.885	56.1
315	.74	.351	6.6	.881	36.2
309	.58	.338	6.2	.879	31.5
302	.36	.322	5.8	.874	22.0
296	.30	.308	5.4	.871	20.7
291	.16	.295	5.0	.869	12.5
286	.20	.278	4.7	.865	17.7
281	.15	.264	4.4	.861	15.0
277	.11	.250	4.1	.859	12.5
273	.132	.239	3.8	.856	17.0
269	.098	.229	3.6	.852	13.9
266	.078	.220	3.4	.850	12.3
262	.089	.210	3.2	.848	15.6
259	.063	.204	3.1	.844	11.8
256	.044	.198	3.0	.841	8.8
253	.085	.194	2.9	.839	18.0
252	.120	.187	2.9	.837	26.7
250	.089	.183	2.8	.835	20.8
247	.041	.180	2.8	.830	9.8
244	.028	.170	2.7	.830	7.3
238	.013	.160	2.7	.820	3.7
234	.009	.150	2.6	.810	2.8

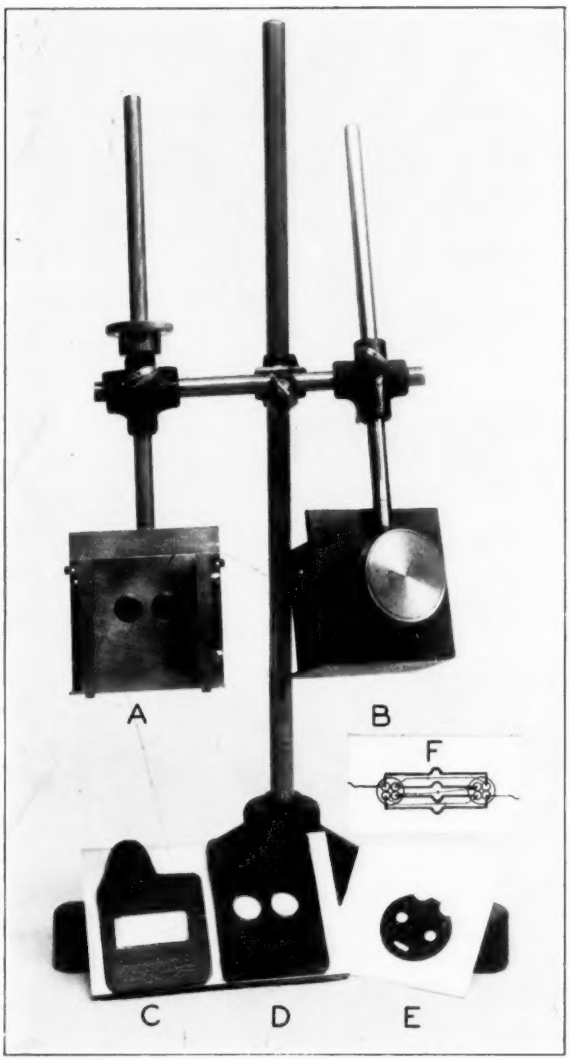

FIGURE 1.—*Balanced thermocouple and filter radiometer*

A, Front view of unfinished mounting; *B*, rear view of an early model; *C*, holder of Noviol A glass; *D*, holder of quartz and barium flint glass filters; *E*, bakelite thermopile mounting; *F*, rear view of balanced thermopile with individual receivers of tin (diameter 1.2 mm, thickness 0.02 mm) attached with shellac varnish to an electrically insulated disk of aluminum (diameter 5.0 mm, thickness 0.01 mm). The insulation is a thin film of cellulose lacquer.

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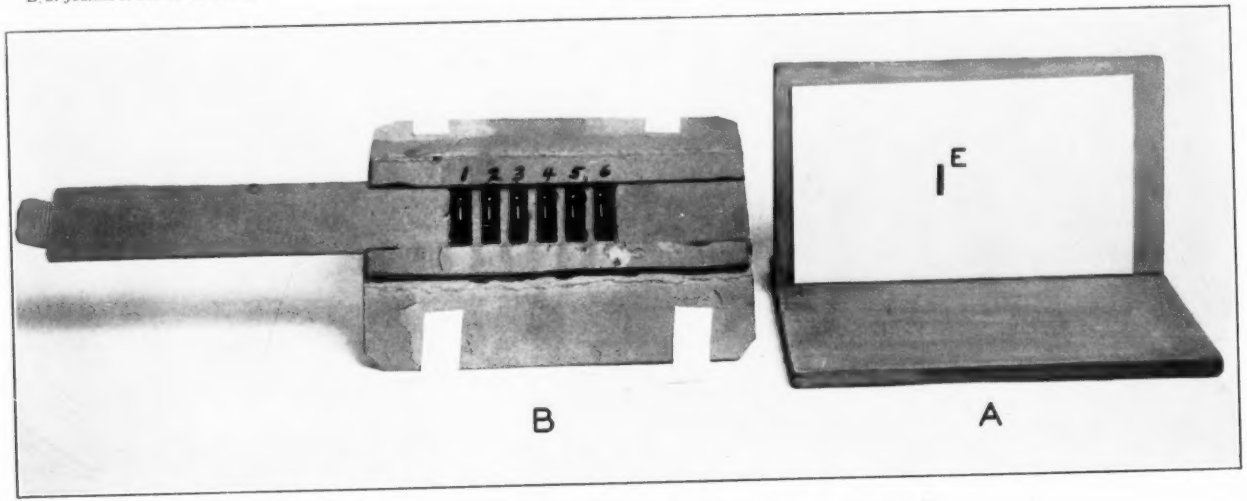

FIGURE 2.—*Arm support A, exit slit E, and arm covering B*

2. DETERMINATION OF THE TOTAL ULTRA-VIOLET RADIANT FLUX OF WAVE LENGTHS LESS THAN 313 mμ IN THE HETEROGENEOUS SOURCE

The total ultra-violet radiation of wave lengths less than 313 mμ was determined, in absolute value, by the balanced thermocouple and filter method (fig. 1) as described on page 740 of the preceding paper (3).

Representative data for the white flame (sunshine) carbon arc are given in Table 2, in which column 1 gives the observed galvanometer deflection on insertion of the filters, and column 3 is the value after correction for the long wave length visible and infra-red radiation transmitted by the Noviol filter.

The most important factor, F, to be determined is the one for evaluating the amount of ultra-violet of wave lengths less than and including 313 mμ relative to the total amount shut out by the barium flint glass exclusion filter. Following the method outlined on page 741 of the preceding paper (3) the sum of the intensities of the wave lengths shorter than and including 313 mμ in column 2 of Table 3, represents the total amount emitted; and column 6 is the total amount excluded by the barium flint glass filter. The ratio of these two summations (252.0/396.3) is the factor $F=0.636$ used in column 4 of Table 2. This factor would, of course, be different for a barium flint glass filter having a different ultra-violet spectral transmission (16) from the one used; but the use of such a filter would change the value in column 1 of Table 2 and, within the errors of observation, would not affect the value sought, which is given in column 6 of Table 3.

As shown in the preceding paper (3) the value of the total ultra-violet of wave lengths less than 313 mμ, obtained by the filter method, is somewhat higher than the value obtained by summation of the spectral measurements. However, from the herein recorded physiological (erythemal) measurements, in which there is no systematic difference between the physiological and radiometric evaluation of the ultra-violet emitted by various sources, it appears that the filter method gives an accurate appraisal of the ultra-violet emitted by the source as a whole, including the reflector. Such an appraisal of the radiation from a lamp and its reflector is not practicable by spectral energy measurements.

TABLE 2.—*Integrated ultra-violet radiation of wave lengths less than, and including 313 mμ, at 30 cm, from a white flame carbon arc, as determined by a balanced thermopile and exclusion filter radiometer*

Observed galvanometer deflection	Infra-red correction	Difference 1-2	Factor F Table 3	Thermopile sensitivity 1 cm= μ w/cm²	Total ultra-violet radiation in μ w/cm²; columns 3×4×5
1	2	3	4	5	6
cm 6.92	*cm* 1.91	*cm* 5.01	0.636	124.6	397.0

TABLE 3.—*Determination of the factor F (used in Table 2) for reducing the observed spectral intensity to radiation of wave lengths less than and including 313 mμ; also the calculated spectral erythemogenic efficiency of a white flame carbon arc*

[The value of the factor F is 252.0÷396.3=0.636]

Wave length	Relative intensity	Transmission quartz minus barium flint	Transmission water cell	Transmission fluorite on thermopile	Radiation excluded by barium flint glass; columns 2×3×4×5	Erythemic response	Erythemic value; columns 2×7
1	2	3	4	5	6	7	8
mμ							
435	238	0.010	0.880	0.900	1.9		
430	240	.011	.880	.900	2.1		
425	242	.012	.880	.900	2.3		
420	243	.013	.880	.900	2.5		
415	244	.015	.880	.900	2.9		
410	244	.018	.880	.900	3.5		
405	244	.020	.880	.900	3.9		
400	246	.023	.880	.900	4.5		
395	251	.027	.880	.900	5.4		
390	255	.030	.880	.895	6.0		
385	216	.035	.875	.895	5.9		
380	178	.040	.875	.890	5.5		
375	150	.050	.875	.890	5.8		
370	129	.055	.875	.890	5.5		
365	108	.067	.875	.890	5.6		
360	94	.090	.875	.890	6.6		
355	78.6	.115	.870	.885	7.0		
350	67	.155	.870	.885	8.0		
345	57	.200	.870	.885	8.8		
340	62	.270	.870	.880	12.8		
335	63	.375	.865	.880	18.0		
330	61	.520	.865	.880	24.1		
325	57	.775	.865	.880	33.6		
320	48	.805	.865	.875	29.2		
315	36.2	.877	.860	.875	23.9	0.00	0.00
310	32.4	.900	.860	.875	21.9	.11	3.56
305	26.2	.900	.860	.870	17.6	.33	8.65
300	21.4	.900	.860	.870	14.4	.82	17.55
295	19.0	.900	.855	.865	12.7	.95	18.05
290	13.3	.900	.855	.860	8.8	.26	3.46
285	17.0	.900	.850	.855	11.1	.09	1.53
280	14.3	.900	.850	.850	9.3	.06	.86
275	14.8	.900	.845	.845	9.5	.07	1.04
270	14.5	.900	.845	.840	9.3	.13	1.89
265	13.3	.900	.840	.835	8.4	.25	3.32
260	13.0	.900	.840	.830	8.2	.42	5.46
255	12.5	.900	.835	.825	7.7	.54	6.75
250	20.9	.900	.830	.820	12.8	.56	11.70
245	8.0	.900	.825	.810	4.8	.57	4.56
240	4.8	.900	.820	.800	2.8	.56	2.69
235	3.0	.900	.815	.790	1.7	.56	1.68
Total.	[1] 252.0				[2] 396.3		[3] 92.75

[1] Total present of wave lengths 313 mμ and less.
[2] Total excluded by barium flint glass filter.
[3] Erythemogenic efficiency=92.75÷252.0=36.8 per cent.

3. DETERMINATION OF THE MINIMUM PERCEPTIBLE ERYTHEMA USING HOMOGENEOUS RADIATION

As already stated there is a wide variation in erythemic susceptibility of the same person under different atmospheric conditions, and of different parts of the body (for example, the inner forearm; see Table 4, W. W. C., January 8, 1932) separated by a distance of only 15 cm or even less. Closely adjacent areas were therefore selected for the

erythema tests. Moreover, the standardization test of the minimum erythemic reaction for homogeneous radiation of wave length 297 mμ was made within a day, or not more than a few days preceding the erythemal tests with heterogeneous radiation from the lamp under investigation.

In view of the necessity of making these two types of erythemal tests, in addition to the quartz-fluorite achromatic lens spectroradiometer for determining the spectral energy data of the lamp under investigation, a large quartz lens and prism spectropyrheliometer (4) was kept in operation for isolating the homogeneous radiation stimulus of wave length 297 mμ, used as a standard. Owing to its high light gathering power, this spectroradiometer (which consists of two plano-convex quartz lenses, 6 cm in diameter, 18 cm focal length, and a 60° quartz prism with faces 6 by 7 cm) transmits a fairly large (0.3 by 10 mm) radiation stimulus of wave length 297 mμ, having a flux of 300 to 350 μw/cm², which produces an erythema in 1 to 3 minutes, depending upon the susceptibility of the skin. In this test, the exposures are made in intervals of 10 seconds, beginning the series with a suberythemal exposure and closing with some of the exposures longer than required to produce a minimum perceptible erythema. From a series of 6 to 8 exposures (some duplicated on different parts of the arm) it is possible to select the exposure giving a minimum perceptible erythema.

TABLE 4.—*Energy of wave lengths less than and including 313 mμ required to produce a minimum perceptible erythema (M. P. E.) using widely different sources of heterogeneous ultra-violet radiation as compared with spectrally homogeneous radiation of wave length 297 mμ, the wave length of maximum erythemogenic effectiveness*

[The ultra-violet radiant flux (u. v. Q.) of wave lengths less than and including 313 mμ, is given in microwatts per cm² (μw/cm²). Region of body exposed: L=left; R=right; F=forearm; U=upper arm]

Source												
λ 297 m μ						The sun						
Observer	Date	u. v. Q. μw/cm²	Time for M. P. E.	Total energy	Region exposed	Dist. from source	u. v. Q. μw/cm²	Time for M. P. E.		Total energy	Erythemogenic efficiency	
								Observed	Calculated		Observed	Calculated
1	2	3	4	5	6	7	8	9	10	11	12	13
	1931		*Seconds*	*Ergs.*		*cm*		*Minutes*	*Minutes*	*Ergs.*	*Per cent*	*Per cent*
W. W. C.	*June* 2	395	90	355, 500	L. U.	.....	90	32	30	1, 728, 000	20. 6	22
R. S.	3	395	120	474, 000	R. F.	.....	78	45	46	2, 106, 000	22. 5	22
J. M. H.	*July* 27	316	60	189, 600	L. U.	.....	69	21	21	869, 400	21. 8	22
W. W. C.	22	316	70	221, 200	L. U.	.....	88	20	19	1, 056, 000	20. 9	22
						General Electric mazda S–1; quartz glass bulb; no reflector						
								Seconds	*Seconds*			
W. W. C.	10	295	60	237, 000	L. U.	20	605	130	125	786, 500	30. 1	31. 4
W. W. C.	17	316	70	221, 200	L. U.	25	387	200	182	774, 000	28. 6	31. 4
J. M. H.	17	316	60	189, 600	L. U.	25	387	170	156	657, 900	28. 8	31. 4

TABLE 4.—*Energy of wave lengths less than and including 313 mμ required to produce a minimum perceptible erythema (M. P. E.) using widely different sources of heterogeneous ultra-violet radiation as compared with spectrally homogeneous radiation of wave length 297 mμ, the wave length of maximum erythemogenic effectiveness*—Continued

Source												
λ 297 mμ						General Electric mazda S-1, corex D bulb; no reflector						
Observer	Date	u. v. Q. μw/cm²	Time for M. P. E.	Total energy	Region exposed	Dist. from source	u. v. Q. μw/cm²	Time for M. P. E.		Total energy	Erythemogenic efficiency	
								Observed	Calculated		Observed	Calculated
1	2	3	4	5	6	7	8	9	10	11	12	13
	1931		*Seconds*	*Ergs.*		*cm*		*Seconds*	*Seconds*	*Ergs.*	*Per cent*	*Per cent*
W. W. C.	*Aug.* 14	316	70	221, 200	L. U.	25	304	270	293	820, 800	26.9	24.8
R. S.	15	295	105	309, 750	L. U.	25	304	420	411	1, 276, 800	24.3	24.8
						"Cold quartz"; mercury glow lamp (hand lamp)						
	July											
W. W. C.	29	316	70	221, 200	L. U.	25	186	210	216	390, 600	56.7	55
J. M. H.	29	316	60	189, 600	L. U.	25	186	180	185	334, 800	56.5	55
						"Cold quartz"; large grid lamp in reflector						
	1932											
W. W. C.	*Jan.* 5	279	120	334, 800	L. F.	92	191	300	319	573, 000	58.4	55
R. S.	5	279	180	502, 200	L. F.	92	191	480	478	916, 800	54.8	55
						General Electric mazda S-2; in reflector						
								Minutes	*Minutes*			
W. W. C.	8	345	135	465, 750	L. F.	62	101	35	36	2, 121, 000	21.9	21.5
W. W. C.	8	345	115	396, 750	L. F.	62	101	30	30	1, 818, 000	21.8	21.5
J. M. H.	8	345	195	672, 750	R. F.	62	101	45	52	2, 727, 000	24.7	21.5
R. S.	8	345	165	569, 250	L. F.	62	101	45	44	2, 727, 000	20.9	21.5
						Quartz mercury arc—uviarc						
	Mar.							*Seconds*	*Seconds*			
W. W. C.	30	342	110	376, 200	R. U.	60	623	165	175	1, 027, 950	36.6	34.4
J. M. H.	30	342	170	581, 400	R. F.	60	623	270	272	1, 682, 100	34.6	34.4
R. S.	30	342	120	410, 400	L. F.	60	623	210	191	1, 308, 300	31.4	34.4
						Carbon arc—Therapeutic B carbons						
R. S.	15	355	135	479, 250	R. F.	50	798	140	143	1, 117, 200	42.9	42.1
J. M. H.	15	347	140	485, 800	L. F.	50	798	140	145	1, 117, 200	43.5	42.1
W. W. C.	17	347	140	485, 800	R. F.	50	798	135	145	1, 077, 300	45.1	42.1
						Carbon arc—Therapeutic C carbons						
R. S.	15	355	135	479, 250	R. F.	50	804	140	143	1, 125, 600	42.6	41.8
J. M. H.	15	347	160	555, 200	R. F.	50	804	160	165	1, 286, 400	43.1	41.8
W. W. C.	17	347	140	485, 800	R. F.	50	804	150	145	1, 206, 000	40.3	41.8
						Carbon arc—sunshine carbons						
R. S.	14	355	135	479, 250	R. F.	50	153	900	851	1, 377, 000	34.8	36.8
J. M. H.	14	347	160	555, 200	R. F.	50	153	960	986	1, 468, 800	37.8	36.8

The "minimum perceptible erythema" is not sharply defined. This is easily demonstrated by wiping the skin with alcohol, on the day following the exposure, which brings out, for an hour or more, weak exposures that previously had shown no visible erythema. On the other hand, by wiping the skin with xylol, weakly visible erythemas may be rendered invisible for a short time. Furthermore, exposures that are a year old, and no longer show pigmentation in daylight, are rendered distinctly visible by the ultra-violet light transmitted through a Corning G986A blue-purple filter.

Nevertheless, in spite of these limitations, it is possible by careful procedure and observation, to procure reliable comparisons of the intensity of ultra-violet radiation of different sources by means of the erythema produced.

The various details in determining the spectral erythemic response of the untanned human skin are described in a preceding paper (5). Briefly stated the exit slit (fig. 2) of metal 0.1 mm in thickness, with beveled edges turned away from the incident radiation in order to obtain a sharp separation, is mounted upon a rigid support, which, after focusing the slit upon the spectral line that is to be isolated, is securely attached to the spectrometer arm. The erythemal and the radiometric measurements are made on the isolated spectral line, just outside the exit slit.

In order to obtain a calibration in absolute value and to increase the accuracy of the determinations of the total energy required to produce a minimum perceptible erythema, the thermopile is temporarily mounted close to and directly over the outside of the exit slit, *E*, in Figure 2 (to completely intercept and measure the intensity of the spectral line after emerging through the slit) and exposed to the standard of radiation. After this calibration is completed, the exit slit is focused upon the spectral line (297 mμ), the support is securely clamped to the spectrometer arm and the energy measurements are made. Immediately thereafter (that is, without moving the lamp, which is necessary in relighting it) the thermopile is removed and the erythemal exposures are made. While this procedure is not absolutely necessary, it is convenient and adds to the accuracy of the work.

The exposures to the homogeneous radiation (as well as the exposures to heterogeneous radiation) were usually made in the afternoon. This permitted observation during the evening and then again the following morning of the erythema produced. For this purpose, each observer carried an index card, containing a record of the identification marks (usually small indelible pencil marks) and notes regarding the time of the exposures. The following day the three observers conferred on the reactions obtained.

From the data on the energy required to produce a minimum perceptible erythema, using homogeneous radiation, a calculation was then made of the time of exposure to the source of heterogeneous radiation, necessary to produce a minimum perceptible erythema. This calculation is based upon the total ultra-violet of wave lengths less than and including 313 mμ, observed by the balanced thermopile and filter radiometer, and based upon the erythemogenic efficiency, which is obtained from the rubescence curve, as explained in a subsequent part of this paper.

4. DETERMINATION OF THE MINIMUM PERCEPTIBLE ERYTHEMA PRODUCED BY HETEROGENEOUS ULTRA-VIOLET RADIATION

The procedure in making the erythema tests using different sources of heterogeneous radiation was more varied than when the exposures were made to homogeneous radiation.

In making the exposures to the sun, the inner, upper, or lower arm was covered with a black cloth containing a series of small rectangular openings, which were covered in succession after definite intervals of exposure.

In order to reduce the heat from the lamp in making the erythema tests on the Mazda S–1 lamp, different parts of the arm were exposed by moving it back of a single slot (0.5 by 10 mm) cut in a large cardboard screen, which was rigidly mounted at a fixed distance from the side of the lamp. Between this screen and the lamp was another screen of white cardboard, to further reduce the heating of the screen and hence the arm.

In the experiments on the Mazda S–2 lamp and the carbon arc lamp, the arm was covered with a cardboard screen (fig. 2) containing six closely adjoining openings (0.5 by 6 mm), which were covered successively by means of a sliding shutter. Close to the end of each slot was a small hole for marking the location of the exposure with an indelible pencil.

Some of the exposures (6 to 8 in all) were purposely made shorter and others longer than the calculated time to produce a minimum perceptible erythema. The short exposures (3 to 4 minutes) differed by intervals of 10 seconds, while for the longer exposures, the intervals were from 1 to 3 minutes.

As mentioned in a previous paper (5) the erythema produced by radiation of wave lengths less than about 270 mμ is superficial and becomes visible within about an hour after exposure. If the exposure is mild, the erythema begins to disappear in the course of 5 hours. On the other hand, the erythema produced by the more deeply penetrating radiation of wave lengths at 297 to 313 mμ, does not become visible before the expiration of 4 to 6 hours and it continues for a day or for many days, depending upon the severity of the exposure.

In sources like the blue flame carbon arc (fig. 4) and the quartz mercury arc, which contain an abundance of short wave length ultraviolet radiation, the erythema appears within about an hour after exposure. Furthermore, depending upon the relative amount of erythemogenic radiation in the two spectral regions (at 250 mμ and at 297 mμ, respectively, see fig. 4) and the total time of exposure, the development of the erythema appears in two stages of maximum redness, caused by the two different rates of growth and decay of the overlapping reactions. While this phenomenon makes it more difficult to define the minimum perceptible erythema, there does not appear to be any definitely observable inhibitory ("antagonistic") or stimulative action of the one spectral region upon the other, in causing an erythema. This conclusion follows from the close agreement between the observed and the calculated erythemogenic efficiencies of the various sources differing widely in spectral distribution of ultra-violet radiation. The slightly higher values observed with the blue flame carbon arc lamp can be ascribed to the lack of exact knowledge of the spectral transmission of the spectrometer

lenses and of the spectral erythemic response for wave lengths shorter than 245 mμ.

III. COMPARISON OF ULTRA-VIOLET INTENSITIES BY RADIOMETRIC AND ERYTHEMAL OBSERVATIONS

While the preliminary data given in the preceding paper (3) seemed sufficient to indicate that the ultra-violet intensity of a source can be determined radiometrically, and that, from the measurements so obtained, the duration of the exposure can be calculated, thus decreasing the hazard of burning the skin, nevertheless it seemed desirable to make a more extensive survey of specific types of sources offered for therapeutic purposes.

1. DETERMINATION OF THE TOTAL ENERGY REQUIRED TO PRODUCE A MINIMUM PERCEPTIBLE ERYTHEMA USING THE STANDARD LINE AT 297 mμ

The chief reasons for adopting homogeneous radiation of wave length 297 mμ (more exactly 2,967 A) as a standard of erythemal and radiometric comparison are (*a*) because this emission line appears to coincide closely with the wave length of maximum erythemic susceptibility, (*b*) because this line is reproducible and easily obtainable in sufficient intensity for erythemal and radiometric measurements (10), and (*c*) because it is easily evaluated in absolute measure by comparison with a standard of radiation (9).

While the intensity of the quartz mercury lamp decreases with usage, the manner of evaluation in absolute units, at the exit slit of the monochromator, presents no obstacles such as would be encountered in attempting to use a source of heterogeneous ultra-violet as a standard of radiation. If an unchangeable source of heterogeneous ultra-violet radiation were available as a standard, all these tedious calibrations would be unnecessary.

In making a comparison of the erythemogenic action of different sources of heterogeneous ultra-violet radiation with that of the standard line (297 mμ) the exposures were made on parts of the inner forearm or on the inner upper arm that had never before been subjected to such erythemal tests; or, at least a year had elapsed since making similar exposure tests.

From the time of exposure, and the intensity, determined in absolute units, as described under Caption II, the total energy required to produce a minimum perceptible erythema is obtained. These data are given in columns 5 and 11 of Table 4.

As shown in column 2 of Table 4 (data of June, 1931, to January 5, 1932) the intensity of the 297 mμ line decreased with aging of the quartz burner (which was used extensively in laboratory measurements); and is much higher for a new burner that was installed in January, 1932. However, as already mentioned, since the source of the homogeneous radiation used in the erythema tests is evaluated at the exit slit of the spectroscope, it is unnecessary to take cognizance of absorption in the spectroscope or change in intensity with aging of the lamp.

2. DETERMINATION OF THE TOTAL ENERGY REQUIRED TO PRODUCE A MINIMUM PERCEPTIBLE ERYTHEMA USING VARIOUS SOURCES OF HETEROGENEOUS ULTRA-VIOLET RADIATION

The flux of radiation of wave lengths less than and including 313 mμ emitted by a heterogeneous source is obtained by the procedure outlined under Caption II. This involves measurements with the filter radiometer and a determination of the spectral energy curve in order to determine the factor *F*.

The time of exposure to produce a minimum perceptible erythema is given in column 9 of Table 4. In this same table, column 8 gives the intensities observed at the point (column 7) of making the exposures. The product of the radiant flux (intensity) and the time of exposure gives the total energy required to produce a minimum perceptible erythema. These energy values are given in column 11 of Table 4.

3. THE ERYTHEMOGENIC EFFICIENCY OF VARIOUS SOURCES OF ULTRA-VIOLET RADIATION

The essential principle involved in evaluating the erythemogenic efficiency is the accurate determination of the total energy required to produce a minimum perceptible erythema, using homogeneous radiation of wave length 297 mμ, as compared with the total energy of wave lengths less than and including 313 mμ required to produce a similar minimum perceptible erythema, when using heterogeneous sources of ultra-violet radiation. In this procedure no recognition is given to the fact that the erythemal reaction to the short wave lengths is more rapid in development and of shorter duration than to the longer wave lengths. In fact, on exposure to heterogeneous radiation (for example, the blue flame carbon arc) having intense emission bands in the region of 250 and 297 mμ, the two erythemic reactions seem to merge; the intensity of the erythema produced by the shorter ultra-violet wave lengths at 250 mμ, decreasing as the intensity of the erythema excited by the longer wave lengths in the region of 297 mμ, is increasing. However, the purpose of the investigation is to establish a method of estimating the intensity of the source and thus avoid burning of the skin by overexposure. This minimum perceptible erythema (that is, one that disappears in less than 24 hours and does not start pigmentation) is merely a useful criterion for indicating the physiological effectiveness of the radiation used.

To derive the erythemogenic efficiency of a heterogeneous source of ultra-violet radiation the ordinates of the observed spectral energy curve are multiplied by the respective ordinates of the spectral erythemic response curve (5). The resulting rubescence curve (see p. 735 and 747 of reference (3)) is analogous, in principle, to the luminosity curve of a source of light (10). The ratio of the shaded areas to the total areas of wave lengths less than 313 mμ, in Figures 3 and 4 is then the calculated erythemogenic efficiency of the source. The close agreement between the calculated erythemogenic efficiency and the experimental values obtained by observing the minimum perceptible erythema produced by the heterogeneous source (using the 297 mμ-line as a standard) is shown in columns 12 and 13 of Table 4.

For completeness in exposition of the subject a brief description is given of each source examined.

(a). THE SUN

In view of the impracticability of observing solar spectral energy curves, under different atmospheric conditions, a standard spectral energy curve was adopted, as explained on page 733 of the preceding paper (3). The rubescence curve is shown in Figure 3. As explained in detail on page 743 of the preliminary paper (3), and as shown in Table 4, the agreement between the observed and the calculated values of the erythemogenic efficiency is as close as can be expected.

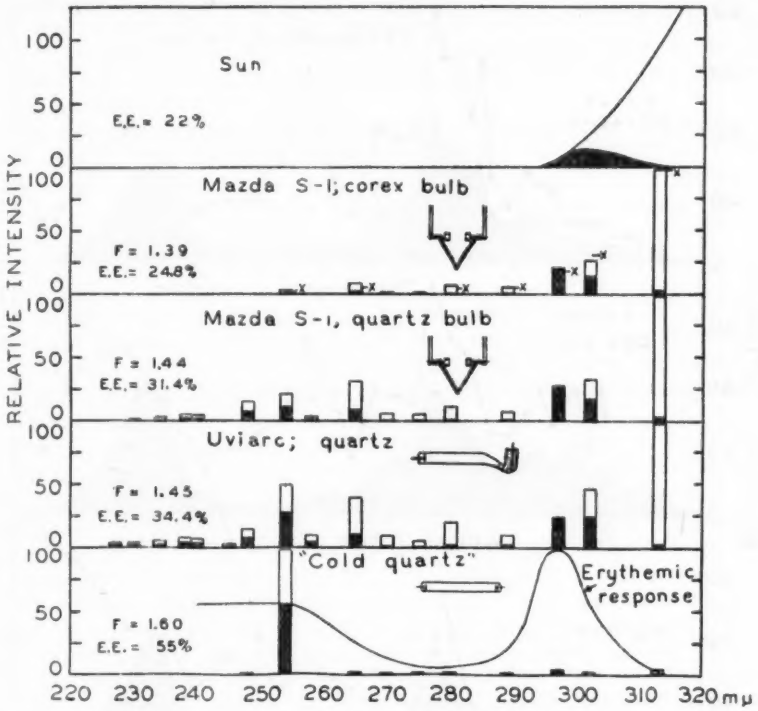

FIGURE 3.—*Ultra-violet spectral energy distribution of various sources; also spectral erythemic response curve of the untanned skin and (the shaded areas) the rubescence energy which is the product of the spectral energy and the spectral erythemic response*

E. E.=erythemogenic efficiency; the ratio of the shaded area to the total area. *F*=factor "*F*."

(b) THE CARBON ARC LAMP

The particular kinds of electrodes used were the white flame ("sunshine"), the blue flame ("therapeutic B"), and the polymetallic cored carbon electrode ("therapeutic C") made by the National Carbon Co. Similar spectral energy measurements on the carbon arc were made some years ago (11).

The electrodes, which were 10 mm in diameter, were operated on 26.5 amperes, 33 volts (across the arc) of an a. c. circuit. They were operated in a horizontal position, in a lamp that was provided with an automatic motor-feed mechanism. Finding that the magnet controls of the feed mechanism affected the galvanometer, the motor-feed device was operated by hand with a double-throw switch for

making the adjustment of the arc length (potential held at 33 volts) when no radiometric readings were in progress.

In order to produce a wide, uniformly irradiated field, a flat aluminum plate, having a finely etched surface, was placed back of the arc.

Under these rigidly controlled conditions, radiometric measurements, made at different times upon different samples and upon different lengths of the same kind of carbons, gave values that were in agreement within less than 1 per cent.

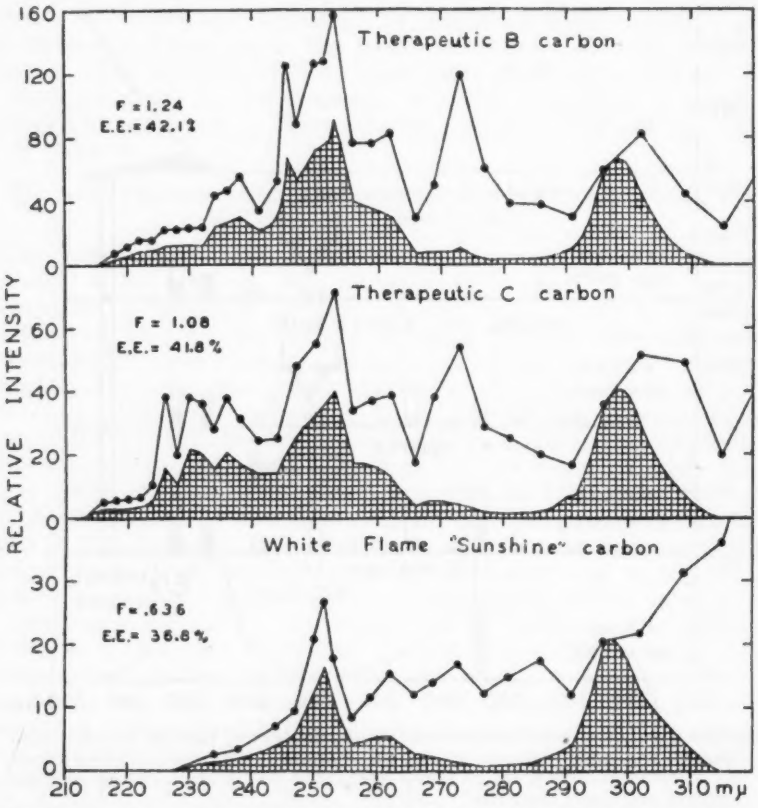

FIGURE 4.—*Spectral energy curves of carbon arcs, and (the shaded areas) rubescence curves which are the product of the spectral energy and the spectral erythemic response*

E. E.=erythemogenic efficiency; the ratio of the shaded area to the total area. *F*=factor "*F*."

The spectral energy curves, observed with a quartz-fluorite achromatic spectrometer, reduced to the normal spectrum and corrected for instrumental absorption as described under a preceding caption, are depicted in Figure 4. The shaded area under the rubescence curve shows the large part of the erythemic effect contributed by the radiation emitted at 240 to 280 mμ, amounting to about 68 per cent of the total in the therapeutic B electrodes.

Attention has already been called to the intense emission in the region of 275 mμ, in the therapeutic C carbon, which may perhaps have a therapeutic action, but does not cause a marked erythema.

(c) THE MERCURY ARC LAMP

Measurements were made of a new type of General Electric Mazda "sun lamp" (types S–1 and S–2) in which the arc discharge occurs at the top of a V-shaped helically wound tungsten filament.

The Mazda S–1 lamp was operated without a reflector. Two models of this lamp were examined (*a*) an experimental lamp in a quartz bulb kindly supplied by the General Electric Lamp Research Laboratory, and (*b*) a commercial lamp in a bulb of Corex D glass, which is intentionally made to be practically opaque to radiation of wave lengths less than about 280 mμ. The measurements were made on the radiation emanating from the side of the lamp, perpendicular to the plane through the V-shaped tungsten filament. The data on these lamps are given in Table 4.

The Mazda S–2 lamp was operated in its reflector. The radiation from this lamp is obtained entirely by reflection. All the observations were made at a fixed distance below the aluminum cap that covers the lower half of the bulb of the lamp. The erythemogenic efficiency and the intensity at a distance of 62 cm (2 feet) below the bulb of the lamp is practically the same as noon day summer sunlight. (See Table 4.)

The spectral energy data on the Mazda S–1 lamp in a Corex D bulb are depicted in Figure 3. The crosses (xxx) indicate averages of similar measurements on 26 lamps, published by Forsythe (12) and his collaborators, showing the good agreement between the two laboratories.

The shaded areas represent the rubescence energy, from which is calculated the erythemogenic efficiency, as illustrated in Table 5 of the preceding paper (3). The slight difference between the values previously published and the new ones given in Table 4 is owing to the adoption of a new spectral erythemic response curve (5), which is considered the most accurate yet determined.

The Uviarc type of quartz mercury arc lamp operates at a high pressure and a high temperature. The type examined is the General Electric 110–volt vertical (Uviarc) lamp operated on 65 volts and about 4 amperes in the burner. Owing to the high current density, the temperature and the pressure are relatively high and the resonance emission line at 254 mμ is practically of the same intensity as the lines at 302 and 313 mμ, in contrast with the so-called "cold quartz" mercury vapor glow lamp (see fig. 3) in which the line at 254 mμ contains over 95 per cent of the radiation emitted by these three lines.

As shown in Figure 3, the spectral energy distribution in the radiation emitted by the commercial (vertical type) Uviarc quartz mercury lamp is not markedly different from that of the Mazda S–1 (experimental) lamp in a quartz bulb. Furthermore, the calculated erythemogenic efficiency in the Uviarc lamp (practically new) is only slightly higher than that of the Mazda S–1 lamp in quartz.

The "cold quartz" ultra-violet lamp is essentially a low vapor pressure, low amperage (0.015 amperes), high potential (5,000 volts, open circuit), glow discharge, similar to the well-known Geissler tube. The power consumed in the so-called cold quartz mercury vapor lamp is small and consequently there is no great rise in temperature of the burner.

The spectral energy distribution of this type of ultra-violet lamp is illustrated in Figure 3. Of the total radiation of all wave lengths less than and including the line at 313 mμ, over 95 per cent (3) is contained in the resonance emission line of mercury vapor at 254 mμ. Two models of this type of lamp were examined—a small grid hand lamp in an aluminum reflector and a large hexagonal-shaped grid lamp in a large aluminum reflector, supported upon a stand for body irradiation.

The erythemogenic efficiency of this type of lamp is high (Table 4), but as shown in Figure 3, practically all the erythemal effect is produced by the line at 254 mμ. The question whether this type of ultra-violet radiation should be used for body irradiation is summarized in another report (13). In a foregoing part of this paper attention is called to the fact that a high erythemogenic efficiency of a source is not necessarily a criterion of its suitability for therapeutic purposes (6).

IV. SPECIFICATION OF MINIMUM INTENSITY AND THE ERYTHEMOGENIC UNIT OF DOSAGE

In view of the ever-increasing number of ultra-violet radiators that are being placed upon the market, some of which emit practically no radiation of wave lengths shorter than 310 mμ (recognized by biologists as having a special therapeutic value) the good agreement between the physiological (erythemal) and the radiometric appraisal of the ultra-violet output of a source finds a direct application in formulating a specification of the amount of ultra-violet that a source must emit in order that it may qualify as a therapeutic agent.

Recently one of the writers (W. W. C.) was called upon by the Council on Physical Therapy of the American Medical Association to obtain information for the purpose of formulating a specification of the amount of ultra-violet radiation that is required for therapeutic purposes.

Based upon a general survey of the problem, involving six distinct summaries of biological and physical data, the conclusion arrived at (2) is that, in order to insure effective therapeutic results, the radiant flux density (intensity) from sources of heterogeneous ultra-violet radiation, of wave lengths less than and including 313 mμ, evaluated according to the spectral erythemic response curve (as recorded in the foregoing pages) should not be less than the erythemogenic equivalent of 20 μw/cm^2 of homogeneous radiation of wave lengths of maximum erythemogenic effectiveness, which wave length, for practical purposes (10), is taken at the emission line of mercury at 297 mμ (more exactly 2,967 A).

As shown in the preceding pages, the emission line at 297 mμ is easily obtainable as a standard source, in sufficient intensity for biological (erythemal) and radiometric tests. Furthermore, the erythemogenic effectiveness of the various sources of heterogeneous radiation, relative to the emission line at 297 mμ, used as a standard is established with a fair degree of precision by the foregoing radiometric and erythemic tests, which indicate an erythemogenic efficiency of about 15 per cent (estimated) for the Mazda CX tungsten filament lamp; 22 per cent for the sun, etc. (See column 13, of Table 4.)

From a study of the data available, it was found (2) that a comfortable operating distance is 75 to 90 cm (2.5 to 3 feet) depending on the source; that for speedy and effective therapeutic results, it is desirable to expose a large area of the nude body (front and back); and that, from a practicable standpoint, the time of a single exposure of any portion of the body should not be continued much longer than 15 minutes. Hence, in formulating a specification, 15 minutes was assumed to be the maximum allowable time of exposure to produce a minimum perceptible erythema on a very sensitive untanned skin.

From the foregoing tests it appears that a 15-minute exposure to a flux density of 20 μw/cm^2, amounting to a total of 180,000 ergs, of wave length 297 mμ, does not produce an erythema on the average person. If the time of exposure is reduced to 10 minutes, then a radiant flux of 30μ w/cm^2 of wave length 297 mμ would be required in order to obtain 180,000 ergs per cm^2.

If the time of exposure is reduced to 1.5 minutes the intensity must be 10 times greater, or 200 μw/cm^2. As indicated in Table 4, all the sources tested physiologically have a radiant flux of this magnitude at a comfortable operating distance from the lamp.

For the various sources of heterogeneous ultra-violet radiation of wave lengths less than 315 mμ, the erythemogenic equivalent of 20 μw/cm^2 of homogeneous radiation of wave length 297 mμ (Table 4) in microwatts per square centimeter, is approximately as follows: The sun $(20 \div 0.22) = 91$; (midday, midsummer, midlatitude, sea level); the Mazda S–1 lamp in Corex D bulb, 80; the Mazda S–2 lamp, 93; the high temperature quartz mercury arc, 58; "cold quartz," low pressure, 36; carbon arcs, 45 to 90 (the latter value is estimated, depending upon the amperage, kind of carbons, kind of window, etc.); and the Mazda CX tungsten filament lamp, 130 μw/cm^2 (estimated).

As already mentioned, in addition to the erythemogenic efficiency, other factors must be considered in connection with the use of a lamp for therapeutic purposes. Hence, the choice among lamps can not be based solely on their erythemogenic efficiency.

It is to be emphasized that this specification of a minimum of 20 microwatts per square centimeter of homogeneous radiation of wave length 297 mμ, or its erythemogenic equivalent of heterogeneous radiation, is the radiant power that is to be applied. The length of time of each exposure, the number of exposures per week, and the total number of exposures (the total energy) required to effect a cure will depend upon the person receiving treatment.

It is important to note that when the sun is used as a source, the intensity can not be increased by decreasing the distance. Hence, it will be necessary to increase the time of exposure. For example, if the ultra-violet intensity (radiant flux density) is only 45 μw/cm^2, then the exposure must be continued twice as long as for an intensity of 90 μw/cm^2.

On the other hand, suppose an artificial source of high intensity is being used; for example, a high intensity carbon arc lamp, having an ultra-violet radiant flux of 180 μw/cm^2 at the standard distance, which is four times the minimum value. It would then be necessary to double the distance in order to reduce the intensity to the standard value, or to reduce the time of exposure to one-fourth the standard value.

The foregoing discussion leads up to the question of what should be the value of the erythemogenic unit of dosage. As indicated elsewhere (14) the numerical value should be some convenient number, neither too large nor too small.

From the data presented in Table 4 it is to be noted that it requires about 200,000 ergs/cm²(200 kiloergs) of homogeneous radiation of the wave length of maximum erythemogenic effectiveness to produce a minimum perceptible erythema. The unit of dosage should, therefore, be some lower value in order to guard against overexposure.

It is suggested that 10,000 ergs/cm²(10 kiloergs) of homogeneous radiation of the wave length 297 mμ (15) be adopted as the erythemogenic unit of dosage of ultra-violet radiation and that it be called the Finsen unit (F. U.). Then, according to this specification, the erythemogenic equivalent of heterogeneous ultra-violet radiation, of wave lengths less than and including 313 mμ, emitted by the above-mentioned sources, would be as follows:

1 F. U. = 10,000 ergs/cm² of the standard wave length, 296.7 mμ, radiation.
= 45,500 ergs/cm² of midday, midsummer, midlatitude, sea level solar radiation.
= 40,000 ergs/cm² of Mazda S–1 lamp radiation.
= 46,500 ergs/cm² of Mazda S–2 lamp radiation.
= 29,000 ergs/cm² of quartz mercury arc (uviarc) radiation.
= 18,000 ergs/cm² of cold quartz radiation.
= 22,500 ergs/cm² to 45,000 ergs/cm² of carbon arc lamp radiation. (The larger value depends upon the kind of carbon and whether the arc is bare or is shining through a glass window.)

From the foregoing correlation of the physiologic and radiometric measurements, it will be evident why most of the published data, now available, appear to be inconsistent and misleading. The published measurements do not include a factor that equates the physiological (erythemal) response. As mentioned above, when this factor is taken into consideration, there is good agreement between the observed and computed times of exposure to produce a minimum perceptible erythema, using sources differing very widely in spectral quality and in total intensity of ultra-violet radiation useful for therapeutic purposes.

In conclusion the following illustration is given of the practical application of the Finsen unit. Let us suppose that, from practical experience, it is found that an irradiation of 20 F. U. per day can be given without producing an overexposure, and that a particular Mazda S–2 lamp, having a radiant flux of 100 μw/cm² (1,000 ergs per second) at the standard operating distance, is available for use. Then, from the above described correlations, it follows that 20 F. U. = 930,000 ergs of Mazda S–2 lamp radiation, and hence, that an exposure of (930,000 ÷ 1,000 =) 930 seconds or 15.5 minutes per day is required.

If it requires 100 exposures of Mazda S–2 lamp radiation to effect a cure, this will amount to a total of 2,000 F. U. This seems simpler than to report the total energy in ergs, which in this instance would amount to 93,000,000 ergs/cm² of Mazda S–2 lamp radiation.

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16. The spectral transmissions of the sample of barium flint glass used in this work may be obtained by subtracting from 0.900 the values given in column 3 of Table 3.

WASHINGTON, April 22, 1932.

RP451

THE ISOELECTRIC POINT OF WOOL

By Milton Harris [1]

Suspensions of solvent-extracted Idaho and Australian raw wool and of scoured worsted cloth in buffer solutions of different pH were prepared by grinding the dry wool to a fine powder and shaking the powder in the buffer solution. Electrophoretic measurements of these suspensions gave an isoelectric point for each wool at pH 3.4.

The samples were slightly different in nitrogen content. If this is indicative of a difference in structure of the wool, the results indicate that the isoelectric point is very slightly or not at all affected by small differences in constitution.

The theory and application of electrophoresis measurements to suspensions of wool are discussed.

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I. INTRODUCTION

The application of physical chemical methods to studies of wool fiber should make it possible to understand better the complex character of this protein as well as offering a means of determining any changes taking place during chemical processing.

Since wool is amphoteric; that is, is capable of ionizing both as an acid and a base, it follows that a study of its acidic and basic nature is of practical as well as theoretical importance. Amphoteric substances are positively charged in acid solution and negatively charged in alkaline solution. The hydrogen ion concentration of a solution in which the ionization of the acid groups of the amphoteric substances, ampholytes, is equal to the ionization of the basic groups is known as the isoelectric point. That is, at this point the concentrations of the cations of the ampholyte equals the concentration of the anions and the sum of their concentrations is a minimum.

A study of the reactions of the wool protein in the isoelectric region is of importance at this time, since more emphasis is being placed on utilization of pH control in wool processing and also because the values of the isoelectric point found by other workers are not in agreement.

It has been shown that it is necessary to control the pH in the treatment of wool during manufacturing processes. Solomone [2] has

[1] Research associate of the American Association of Textile Chemists and Colorists.
[2] G. Solomone, The pH in the Treatment of Wool, Boll. laniera, vol. 43, pp. 892–897, 1931.

pointed out that there are optimum pH values for the scouring, oiling, bleaching, and dyeing of wool. A specific example is brought out in the chlorination of wool. If this operation is carried out in the isoelectric region, the attack on the fibers is reduced to a minimum.

The isoelectric point has been reported as low as pH 3.4 and as high as pH 4.8. Meunier and Rey[3] determined the point of minimum swelling of wool fibers immersed in buffer solutions of varying pH, and found the isoelectric point at pH 3.6 to pH 3.8. Marston[4] investigated the amount of acid bound in the region of the isoelectric point. By extrapolating the curve relating the amount of acid bound with the pH of the reacting system, he found that the point at which no acid is bound lies in the region of pH 3.4. Speakman[5] treated samples of wool with standard potassium ferrocyanide solutions of known pH. After 24 hours the wool was removed and carefully washed to remove uncombined ferrocyanide and then immersed in ferric chloride solution. By this procedure he found that when the pH was high no combination with the ferrocyanide ion occurred; at pH 4.8, combination began and thereafter the amount of Prussian

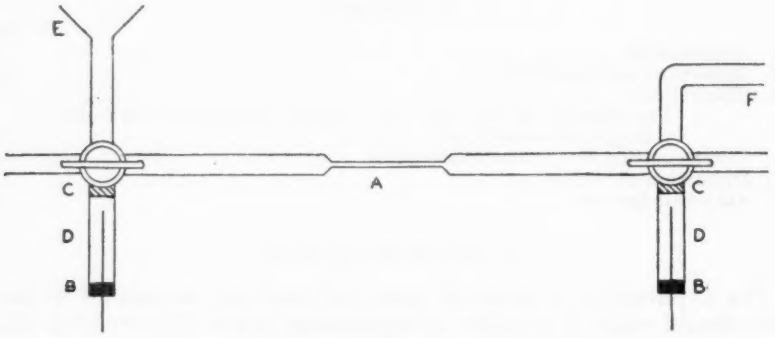

FIGURE 1.—*Electrophoresis cell*

blue formed increased as the pH decreased. He concluded from this that the isoelectric point of wool is in the neighborhood of pH 4.8.

A number of methods are available for the determination of the isoelectric points of proteins, but the applicability of any specific method depends largely on the nature of the protein in question. These methods are based on the fact that at the isoelectric point, the osmotic pressure, viscosity, amount of alcohol required for precipitation, conductivity, swelling, and migration in an electric field are all a minimum.

The insolubility of wool in ordinary solvents has limited the number of these methods which can be used in studying this material. Since microscopic suspensions of wool are easily prepared, it is possible to study the migrations of the particles in an electric field. The movement of small particles suspended in a liquid in which a potential difference between two electrodes has been set up is known as electrophoresis.

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[3] Meunier and Rey, "Sur les Propriétés de la laine," J. Soc. Leather Trades Chemists, vol. 11, p. 508, 1927.

[4] Marston, the Chemical Composition of Wool, Council Sci. & Ind. Res. Australia, Bull., vol. 38, 1928.

[5] J. B. Speakman, the Behaviour of Wool as an Amphoteric Colloid, J. Soc. Dyers and Colorists, vol. 41, p. 172, 1925.

II. APPARATUS AND METHODS

The electrophoresis cell (fig. 1) employed in this work is similar to the one described by Northrup[6] and is exactly like the one used by Abramson.[7] *A* is made of fused glass with approximate dimensions as follows: Length 3.5 cm, width 1 cm, and thickness 0.055 cm. The diameter of the connecting side tubes is large in comparison with the thickness of the cell. The electrodes, *D D*, are nonpolarizable and composed of $Cu/CuSO_4$. *C C* are porous plugs prepared as follows: Powdered gypsum is put into the electrode vessels, sufficient water added, and the mixture is allowed to dry and harden for several hours. The apparatus is filled with saturated potassium chloride solution and allowed to stand until the pores of the plaster of Paris plugs are saturated with electrolyte.

The stopcocks are turned so that *A* is open to *E* and *F*. The suspension to be studied is poured into *E* and both stopcocks turned so that *A* is open to *D D*. The apparatus is placed on the platform of a microscope and a direct current of 220 volts is applied to the electrodes. The current is reversed by means of a commutator. The microscope is equipped with an 8 mm objective and a 6X eyepiece. The eyepiece contains a scale which covers 0.34 mm on the stage micrometer.

The electrophoretic velocity (see Sec. III) was measured in each direction and an average of 10 readings was taken.

In the determination of the isoelectric point, three samples of wool were used, namely, raw Idaho wool, raw Australian wool, and wool from a piece of worsted cloth which had not been carbonized. The wool grease and dirt were removed from the raw wool by successive extractions with Stoddard solvent (boiling range 150° to 200° C), alcohol, and ether until no appreciable residue was obtained on evaporation of the solvent. The worsted cloth was scoured in a half per cent soap solution after which it was carefully washed with water, alcohol, and ether to remove any traces of soap and oils remaining.

The purified wool was ground in a Wiley mill until the powder formed passed through a 100-mesh sieve. The powder was shaken with water and the larger particles allowed to settle to the bottom after which the upper portion was decanted. The finer particles remained suspended in the liquid for several hours.

The buffers were prepared according to Clark[8] and the final pH determined by employing the quinhydrone electrode. The buffer mixtures used were as follows: pH 1.4 to 2.2, potassium chloride-hydrochloric acid mixture; pH 2.4 to 3.8, acid potassium phthalate-hydrochloric acid mixtures; pH 4.0 to 6.0, acid potassium phthalate-sodium hydroxide mixtures.

III. THEORETICAL

When the movement of suspended particles is observed in successive layers from top to bottom of a cell as has just been described, it will be seen that particles in the layer next to the glass move toward the cathode as if they were positively charged. By observing layers from the glass toward the center of the cell, a layer will be found where

[6] J. Northrup, The Stability of Bacterial Suspensions, J. Gen. Physiol., vol. 4, p. 629, 1922.
[7] H. Abramson and H. Freundlich, Uber die Kataphoretische Wanderings-geschwindigkeit gröbere Teilchen in Solen und Gelen, Z. Phys. Chem., vol. 128, pp. 25-38, 1927.
[8] W. M. Clark, The Determination of Hydrogen Ions Williams and Wilkins, pp. 106-107.

there is no apparent movement. Below this point, the direction of migration on the particles reverses and their velocity increases until the center is reached.

Since there is a movement of the liquid with respect to the glass wall of the cell as the result of an applied electromotive force, it follows that the liquid must be oppositely charged with respect to the wall. Apparently a double electric layer exists at the interface of liquid and wall, the water being positive and the glass surface negatively charged.

The movement of liquids and suspended particles in flat electrophorsesis cells has been investigated by numerous workers. Ellis[9] assumed that for a flat cell of depth X

$$Vobs = V_p + V_w$$

where

$Vobs$ = The observed electrophoretic velocity of the particle.
V_p = The velocity of the particle relative to the liquid.
V_w = the velocity of the liquid.
In the layer where $V_w = 0$, $Vobs = V_p$.

In his theoretical considerations Von Smoluchowski[10] has shown that the layers at which the velocity of the liquid is zero are located at approximately one-fifth and four-fifths of the depth of the cell from the top. That is

$$V_p = V_{1/5} = V_{4/5} = 1/x \int_0^X Vobs\, dx$$

where x is the depth in the cell. He also showed that the velocity of a particle in either layer is equal to three-fourths of the observed velocity of a particle in a layer one-sixth of the depth from the top plus one-fourth of the observed velocity of a particle in a layer at one-half of the depth.

Experimental work of Ellis and of Svedberg and Anderson[11] have confirmed this theory for flat cells from 50 μ to about 1.0 mm in thickness.

In order to determine that the cell used conformed to this theory Vobs was measured at successive levels in the cell and V_p was obtained by graphical integration. Crude quartz powder was purified as described by Abramson,[12] and suspended in distilled water. The movement of the suspended particles in the electrophoresis cell is shown in Figure 2. The shape of the curves depends on the pH of the solution. By graphical integration it was found that the theory of Von Smoluchowski was applicable to the cell used in this work.

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[9] R. Ellis, Die Eigenschaften der Olemulsionen, Z. Physik., Chem., vol. 78, p. 321, 1912.
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[11] T. Svedberg and H. Anderson, Zur Messmethodik der Electrischen Kataphorese, Kolloid Z, vol. 24, pp. 156–165.
[12] H. Abramson, Electrokinetic Phenomena, J. Gen. Physiol, vol. 13, p. 171, 1929.

1. THE INFLUENCE OF SIZE AND SHAPE OF WOOL PARTICLES ON THEIR ELECTROPHORETIC MOBILITY

The electrophoretic velocity V of a particle relative to a given medium is

$$V=\frac{1}{4\pi}\cdot\frac{XD\zeta}{n} \tag{4}$$

Where

X = field strength.
D = dielectric constant of the liquid.
ζ = electro-kinetic potential.
n = viscosity of the liquid.

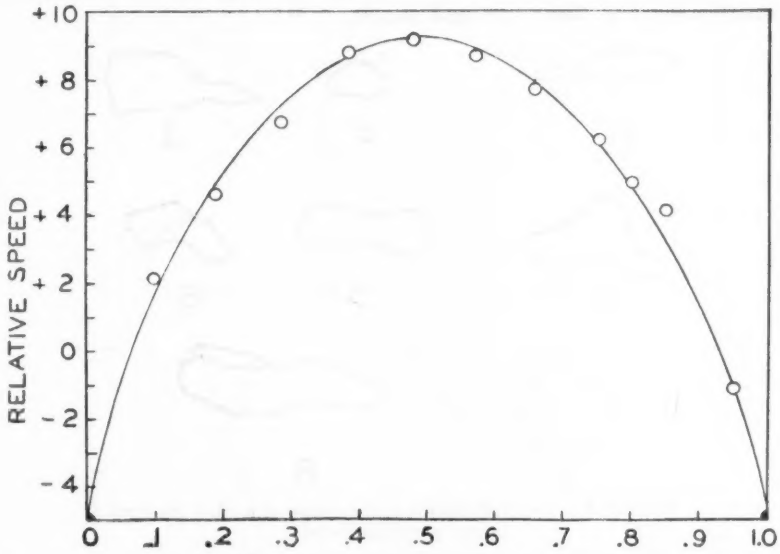

FIGURE 2.—*Velocity—level curve for the electrophoresis cell used in the experimental work*

This relationship was first developed by Helmholtz [13] and later extended by Perrin and Von Smoluchowski.[14]

This equation predicts that the electrophoretic velocity is independent of the size and shape of the particle. Abramson [15] has summarized experiments which confirm this. The experiments indicate that the electrophoretic mobility of solid particles like quartz, glass particles, asbestos needles, and tyrosine needles is independent of size and shape in the size ranges indicated.

A sample of wool prepared as previously described was suspended in a dilute buffer solution at approximately pH 4.8. The particles varied in size from about 5 to 30 μ. The time required for different sizes and shapes of particles to move across the field was measured. The general outline of the shape and the relative size of each of the

[13] H. Helmholtz, Studien uber Electrische Grenzschichten, + Wied Ann, vol. 7, 337–383, 1879.
[14] See footnote 9, p. —.
[15] H. Abramson, Influence of Size, Shape, and Conductivity on Cataphoretic Mobility, J. Phys. Chem., vol. 35, pp. 289–308, 1931.

particles noted is shown in Figure 3 while the corresponding time required to cross the scale is given in Table 1.

TABLE 1.—*Relative speed of wool particles*

Particle	Time
	Seconds
1	14.1
2	14.3
3	13.6
4	13.9
5	14.1
6	13.6
7	13.9
8	13.5

The results in Table 1 indicate that the mobility of the wool particles is independent of their size and shape.

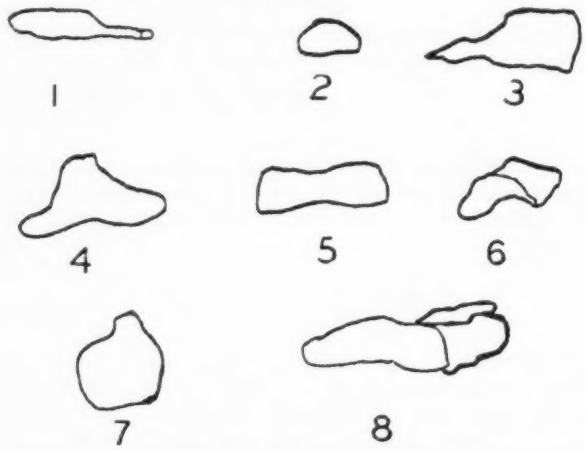

FIGURE 3.—*General outline of the shape of each of the various particles noted*

They are drawn to approximately the same scale. (Two dimensions.)

IV. DETERMINATION OF THE ISOELECTRIC POINT

Suspensions of wool in buffer solutions of known pH were prepared as described in an earlier part of this paper and the electrophoretic velocities of the wool particles determined.

TABLE 2

pH	μ/sec./volt/cm				Average percentage deviation from mean
	Idaho wool	Australian wool	Worsted cloth	Average velocity	
1.54	+2.50+2.30+2.38	+2.44+2.50+2.38	+2.32	+2.40	2.91
1.93	+2.20+2.22+2.21	+2.29+2.27+2.18	+2.16	+2.22	1.70
2.30	+2.08+2.03+2.04	+2.16+2.08+2.16	+2.04	+2.08	2.11
2.52	+1.93+1.86+1.90	+1.93+1.96+1.93	+1.89	+1.93	1.36
2.91	+1.32+1.24+1.23	+1.40+1.28+1.38	+1.31	+1.32	3.92
3.31	+.48+.46+.47	+.52+.50+.52	+.54	+.50	6.26
3.48	−.54−.61−.58	−.55−.51−.61	−.62	−.58	4.84
3.64	−.94−.89−1.00	−1.03−.98−.99	−1.03	−.98	3.98
4.11	−1.42−1.25−1.39	−1.50−1.46−1.45	−1.42	−1.41	3.56
4.63	−1.86−1.90−1.95	−1.90−1.98−1.94	−1.98	−1.93	1.94
5.47	−2.61−2.50−2.46	−2.46−2.51−2.48	−2.45	−2.52	1.74
Average					3.12

The observed velocities are given in Table 2 in which each figure is the average of 10 observations. These data are plotted in Figure 4 which shows the shape of the pH mobility curve. The value assigned to the isoelectric point from this curve is pH 3.4.

The accuracy of this value depends upon the accuracy of the measurements of the pH and of the velocity of the wool particles. The error in the determination of the velocities, although comparatively large, is practically negligible because of the steep slope of the curve in the isoelectric region. Since the pH is known to be accurate to

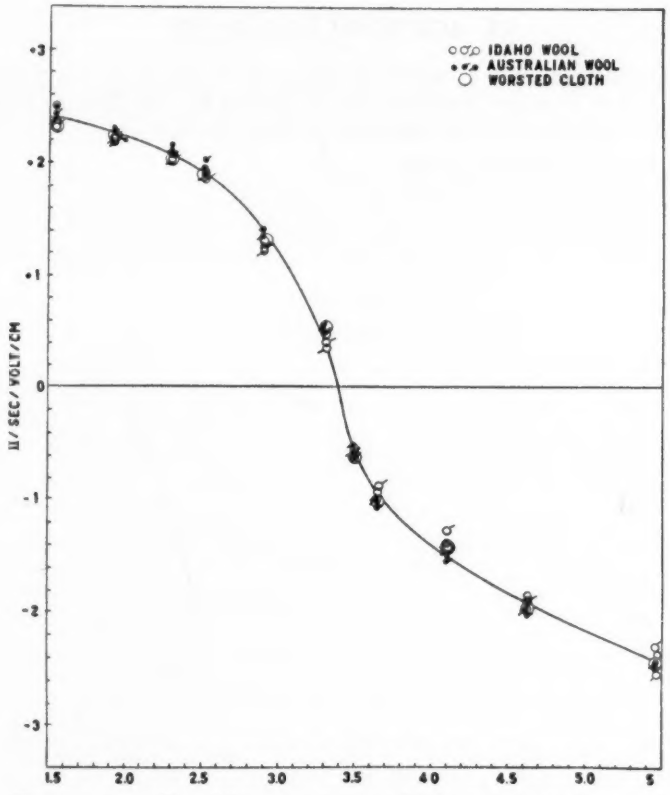

FIGURE 4.—*pH mobility cure for raw Idaho and Australian wool and for worsted cloth*

± 0.05, this may be taken as the limiting error for the isoelectric point of wool.

V. DISCUSSION OF RESULTS

The isoelectric point 3.4 obtained from the pH mobility curve is in good agreement with the value 3.4 obtained by Marston [16] and the value 3.6–3.8 obtained by Meunier and Rey.[17] The results of the individual measurements on the raw Idaho and Australian wool and the worsted cloth are also in good agreement with each other.

[16] See footnote 4, p. 780.
[17] See footnote 3, p. 780.

Analyses of the samples for total nitrogen gave the following values:

	Per cent nitrogen
Australian wool	16.19
Idaho wool	16.48
Worsted cloth	17.16

Assuming that this variation in nitrogen content is some indication of a variation in structure, the results of the electrophoretic measurements confirm the theory that the isoelectric point is only slightly or not at all affected by small differences in structure.

VI. ACKNOWLEDGMENT

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WASHINGTON, April 1, 1932.

AN OPTICAL METHOD FOR MEASURING TEMPERATURE DISTRIBUTION AND CONVECTIVE HEAT TRANSFER

By R. B. Kennard

ABSTRACT

In order to avoid the errors inherent in material thermometers, a method has been devised whereby the temperatures in the region of heated air near a hot surface may be determined from the displacement of the fringes in an interferometer.

Photographs were taken of the interference fringes near a hot vertical plate and near horizontal heated cylinders. The temperature distribution and the convective heat transfer were determined from measurements made on enlargements of these photographs. It is shown that the temperature distribution does not correspond to that called for by the film theory.

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I. INTRODUCTION

The exchange of heat between the surface of a solid and a fluid in contact with it is one of the most important types of heat transfer. A complete mathematical solution of the problems involved must combine the hydrodynamic laws for the motion of a viscous fluid in both laminar and turbulent flow, with Fourier's laws of heat conduction. Because of the extreme complexity of the problem no complete solution has as yet been made. Many theoretical workers have sought approximate solutions by making arbitrary assumptions. To avoid the mathematical difficulties involved in the analysis of turbulent flow, the first approximation is to consider the problem as involving laminar flow only. The combination of the laws of lami-

nar flow and heat conduction is further simplified by assuming a non-viscous fluid. This method was followed by Boussinesq [1] and Russell.[2] The calculated results, however, differ widely from those observed experimentally, and the method is of little value in the direct calculation of heat transfer.

The method of dimensional analysis [3 4 5 6] has been of great value in extending the use of experimental data on convective heat transfer, but does not indicate what takes place in the boundary region between the solid and the fluid.

In calculating the heat transferred by convection, it is generally assumed that the heat is transferred by conduction through a thin film of fluid in contact with the solid. On one side of this film the temperature is that of the surface of the solid, and on the other side that of the fluid at a great distance. The thickness of such a film may be calculated from measurements of (*a*) the total heat transferred by convection, (*b*) the total temperature drop, and (*c*) the average thermal conductivity of the fluid. The conducting film as defined in this manner is purely hypothetical. However, since the thickness of the film is in fact not known, it is the practice to combine the thickness and thermal conductivity into the film coefficient [7] h

$$h=\frac{K}{L}$$

where K is the conductivity and L the film thickness. These film coefficients, or coefficients of heat transfer, determined experimentally over a wide variety of conditions, can be adapted to particular problems by the methods of dimensional analysis.

The film hypothesis was placed on a theoretical basis by Langmuir.[8 9] He assumed that near the surface the flow would be laminar, with the velocity increasing from zero at the surface to a maximum critical velocity. When the critical velocity was exceeded, the flow would break into turbulent motion. Langmuir assumed that because of this turbulence the temperature throughout the turbulent region would be essentially the same as that of the ambient fluid at a great distance. In other words, this theory would lead to the conclusion that the temperature drop would be confined to the region of laminar flow. Reasoning from the kinetic theory of gases, and taking into account the change of viscosity and heat conductivity with temperature, Langmuir deduced certain laws for the thickness of this film. From these laws it was possible to correlate the observations of many observers on convective heat transfer for wires and cylinders in different gases. The correlation was remarkably good over a wide range of pressures and temperatures of the gas, and of cylinder diameters.

In order to determine how closely the film theories agree with the physical facts, it is necessary to measure the temperature and the

[1] Boussinesq, Comptes Rendus, vol. 132, p. 1383, 1901.
[2] Alex. Russell, Phil. Mag., vol. 20, p. 591, 1910.
[3] Buckingham, Phys. Rev., vol. 4, p. 345, 1914.
[4] Davis, Phil. Mag., vol. 40, p. 692, 1920; vol. 41, p. 899, 1921.
[5] Rice, Trans. A. I. E. E., vol. 42, p. 653, 1923.
[6] Fishenden and Saunders, Engineering, vol. 130, p. 177, 1930.
[7] Walker, Lewis, and McAdams, Principles of Chemical Engineering (2d ed.), pp. 134–154.
[8] Langmuir, Trans. A. I. E. E., vol. 31, pt. 1, p. 1229, 1912.
[9] Langmuir, Trans. A. I. E. E., vol. 32, p. 301, 1913.

velocity distribution in the fluid near the hot surface. Griffith and Davis [10] made such an investigation for free convection in air in front of a vertical hot plate. Jürges,[11] Ludowici,[12] and Elias [13] made a similar study for forced convection. In these investigations, the air velocities were measured by a hot wire anemometer, and the temperatures either by the resistance of a fine platinum wire [10] or by thermocouples.[11 12 13]

There are inherent objections to the introduction of any material thermometers under these conditions. The effects of radiation and the conduction of heat along the leads may cause the temperature of the thermometer to differ materially from that of the air surrounding it. Furthermore, the introduction of any stationary solid into a moving fluid will disturb the conditions of temperature and flow. In the case of small wires this disturbance decreases only very slowly with the diameter, for, at the surface of the wire, regardless of its size, the velocity of the fluid is reduced to zero. There is therefore a

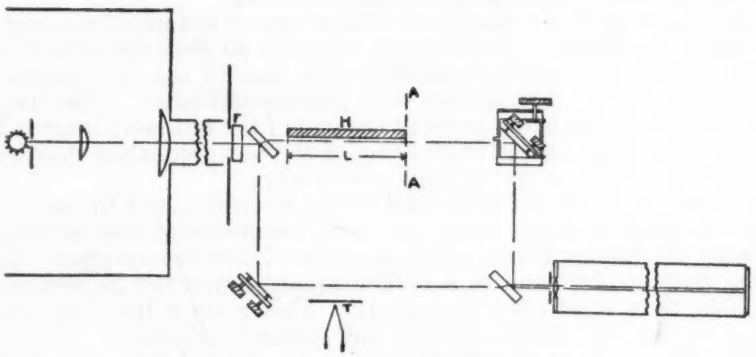


FIGURE 1.—*Experimental arrangement*

H is the heated plate or cylinder of length *L*. *AA* is the plane in which the fringes were brought to a virtual focus. *F* is a filter which transmits only the green mercury light. *T* is a shielded thermal couple

limit to the advantage gained by using extremely fine wires as resistance thermometers or as thermocouples.

II. METHODS AND PROCEDURE

In order to avoid the errors incident to the use of material thermometric devices the following method has been devised whereby the temperature distribution in the air near a heated surface may be determined by the displacement of the fringes in an interferometer.

The experiments were performed in an inside basement room, the walls and ceiling of which were lined with 4 inches of cork. There were, therefore, no complications caused by vibration, or by stray convection currents set up by unequal temperatures within the room.

In Figure 1 is shown a plan view of the interferometer together with the light source, the heated surface, and the camera.

[10] Griffith and Davis, Food Investig. Board, No. 9, 1922.
[11] Jürges, Gesundheits Inginewr, vol. 19, p. 5, 1924.
[12] Ludowici, Z. d. V. D. I., vol. 70, p. 1122, 1926.
[13] Elias, Z. f. Ang. Math. u Mech., vol. 9, p. 434, 1929. Elias, Z. f. Ang. Math. u Mech., vol. 10, p. 1, 1930.

The light from a mercury lamp passing through a 10 mm aperture is brought to a slightly convergent beam by two condensing lenses. The use of two lenses is found convenient as the focal length of the combination can be varied by moving the inner lens, and in this way the degree of convergence of the light beam can be controlled without moving the lamp or the large outer lens. The lamp and lenses are housed in a light-tight cabinet separated from the interferometer by a 60 cm tube. This was done in order to reduce the effect of stray air currents caused by the heat of the lamp. At the end of the tube is a shutter so that the light of the lamp can be cut off completely. Before entering the interferometer the light passes through a Wratten 77 filter F, which will transmit only the mercury green light.

A Zehnder interferometer was chosen, as the path of light goes past the hot surface only once, as compared to twice for the Michelson instrument. For the same temperature rise and the same fringe shift the width of the heated surface could be made twice as great and the end corrections proportionally reduced.

The heated body H was placed in one arm of the interferometer as shown in the figure. The set was adjusted so that the axis of the beam of light accurately coincided with that of the interferometer and passed by the hot surface with grazing incidence. The fringes were brought to a virtual focus at the end of the hot body nearest the camera (line AA), except in the case of the hot wire when they were brought to a focus at the middle of the wire.

In order to avoid any distortion of the interferometer by radiation from the heated body, water at room temperature was syphoned through the hollow frame which is made of 2-inch iron pipe. This frame rests on dry sand in a hollow square supported 34 inches off the floor by a rigid open framework. This gives a free flow of air about the heated surface without any chimney effects.

The camera has a length from lens to plate of 136 cm. A 2½-diopter spectacle lens is used for the objective, giving a magnification of 2.4 diameters. Enlarged positives were made from the negatives, the total magnification being approximately 7 diameters.

In taking all photographs a double exposure was made on the same plate to show a millimeter scale in the object field. The temperature distribution was determined from the displacement of the fringes and the dimensions as obtained from the photograph of the scale.

Figures 5, 7, 9(A), 9(B), and 11 show the type of photographs of interference fringes that may be taken with this instrument.

III. CALCULATION OF RESULTS

1. GENERAL

Let A and B (fig. 2) be two adjacent interference fringes formed by monochromatic light passing through the column of air adjacent to the heated surface H. If the temperature were uniform throughout, the center line of fringe A instead of the center line of fringe B would pass through the point P. The shift of one fringe at the point P indicates that there is one less wave of light in the path through P than there would be if the temperature at P were the same as at Q.

The temperature of the air is obtained from its density which is related to the refractive index by the Lorenz-Lorentz equation [14]

$$\frac{n^2-1}{n^2+2}=C\rho \tag{1}$$

where n is the index of refraction, ρ the density, and C is a constant characteristic of the fluid.

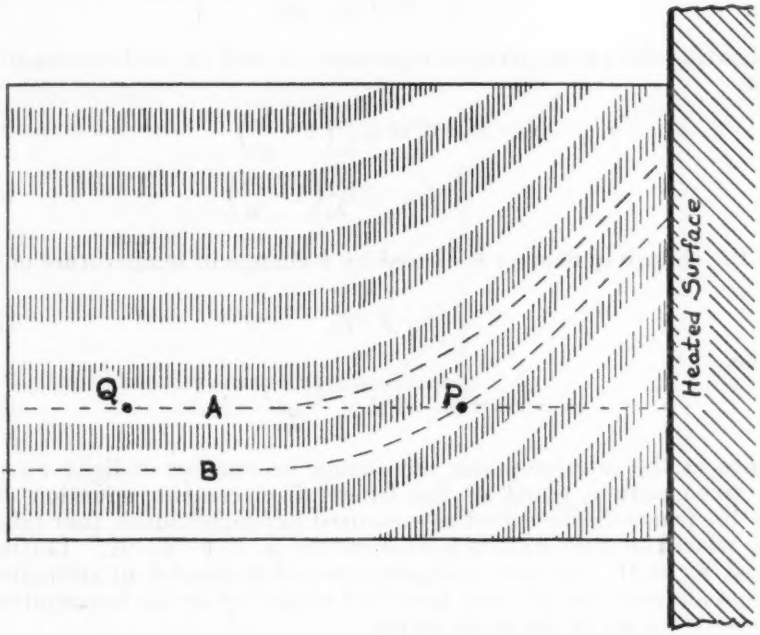


FIGURE 2.—*Method of measuring temperature from fringe shift*

Since the index of refraction of air under the prevailing experimental conditions is of the order of 1.0003 the above equation reduces very closely to

$$(n-1)=3/2C\rho \tag{2}$$

If, under one set of conditions, N_1 and n_1 are the number of light waves over a given path, and the index of refraction, respectively, and N_2 and n_2 are the same quantities under a second set of conditions then

$$n_1=\frac{N_1}{N_0}$$
$$n_2=\frac{N_2}{N_0} \tag{3}$$

where N_0 is the number of light waves in the same path in a vacuum. If L is the length of path under consideration, which is that of the

[14] Lorentz, The Theory of Electrons, p. 145, 1909.

heated surface L_0 plus a small end correction ΔL, and if λ_0 is the wave length in vacuum of the light used then

$$N_0 = \frac{L}{\lambda_0} \tag{4}$$

From equation (2) the change of index of refraction for a given change in density is

$$n_1 - n_2 = 3/2C(\rho_1 - \rho_2) \tag{5}$$

Inserting the values given in equations (3) and (4) and rearranging yields

$$\begin{aligned} N_1 - N_2 &= 3/2C\rho_1 \frac{L}{\lambda_0}\left(1 - \frac{\rho_2}{\rho_1}\right) \\ &= (n_1 - 1)\frac{L}{\lambda_0}\left(1 - \frac{\rho_2}{\rho_1}\right) \end{aligned} \tag{6}$$

If the change in density is caused by a change in temperature only

$$\frac{\rho_2}{\rho_1} = T_1/T_2 \tag{7}$$

whence

$$N_1 - N_2 = (n_1 - 1)L/\lambda_0 \frac{T_2 - T_1}{T_2} \tag{8}$$

Since in the interferometer the change in number of light waves in a given path is equal to the fringe displacement, equation (8) gives the fringe displacement as measured in fringe widths, that takes place when the temperature is changed from T_1 to T_2 °K. Letting T_1 and n_1 be the absolute temperature and the index of refraction or room air, equation (8) may be solved explicitly for the temperature rise above the air of the room giving

$$T_2 - T_1 = T_1 \frac{\Delta N}{(n_1 - 1)L/\lambda_0 - \Delta N} \tag{9}$$

The quantity $(n_1 - 1)$ is given in International Critical Tables [14] for standard conditions and may be calculated for any conditions by using the gas laws, making proper correction for humidity.[15]

2. END CORRECTION

As previously mentioned the length $L = L_0 + \Delta L$ includes the length of the heated surface L_0 plus a small correction ΔL which takes into account the fact that the layer of heated air extends beyond the ends of the hot surface. It was found that when no allowance was made for this end correction the temperature rise as calculated for the air at the surface of a 103 mm plate was greater by 5 per cent than the observed temperature rise of the plate itself.

If in equation (9) we insert for T_2 the observed temperature of the plate and for ΔN the observed fringe displacement at the plate surface, and solve for L, we find that $\Delta L = 5$ mm $\pm$ ½ mm. This value holds for all four cases under consideration as shown by the

[14] I. C. T., vol. 7, pp. 4 and 5.

following values of $T_2 - T_1$ at the plate surface as calculated from the observed fringe displacement at the plate.

$(T_2 - T_1)$	
Observed	Calculated
° C.	° C.
118.1	118.9
63.5	63.8
29.4	29.4
14.3	14.3

This method of calculating ΔL at the surface of the plate neglects any discontinuity of temperature between the plate and the air at its

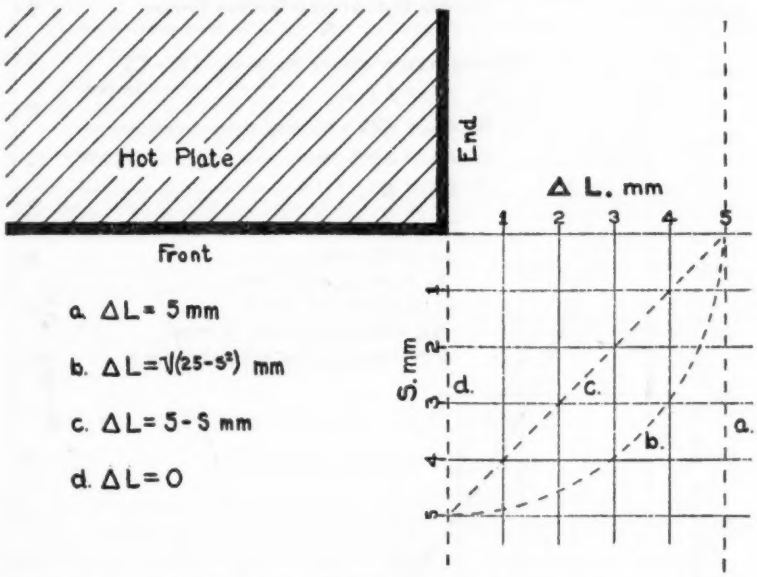


FIGURE 3.—*Variation of the end correction with distance from the plate on several assumptions*

surface. Although the kinetic theory indicates the existence of such a discontinuity it is so small that it can be entirely neglected under the conditions of these experiments.

Having determined the value of ΔL at the surface of the plate there remains the problem of determining its approximate value at any point in the region of heated air. As the quantity involved is small, a purely empirical solution was considered sufficient. As one limit (fig. 3) let us assume (*a*) that $\Delta L = 5$ mm remains constant throughout this region. For another limit let us assume (*c*) that ΔL decreases linearly to zero at some point, say for convenience 5 mm in front of the plate. Between these two limits a circle (*b*) has been arbitrarily drawn. For any given distance in front of the plate, ΔL was chosen as the corresponding semichord of this circle in the final computation of the results.

In Figure 4 is shown the average displacement of the center line of the interference fringes for a total temperature rise of 118.1° C. as measured from the photograph in Figure 5. The scale for ΔN in fringe widths is shown on the right and that for temperature rise on the left. These scales have been so chosen that the fringe displacement at the plate coincides with the temperature rise at the same point.

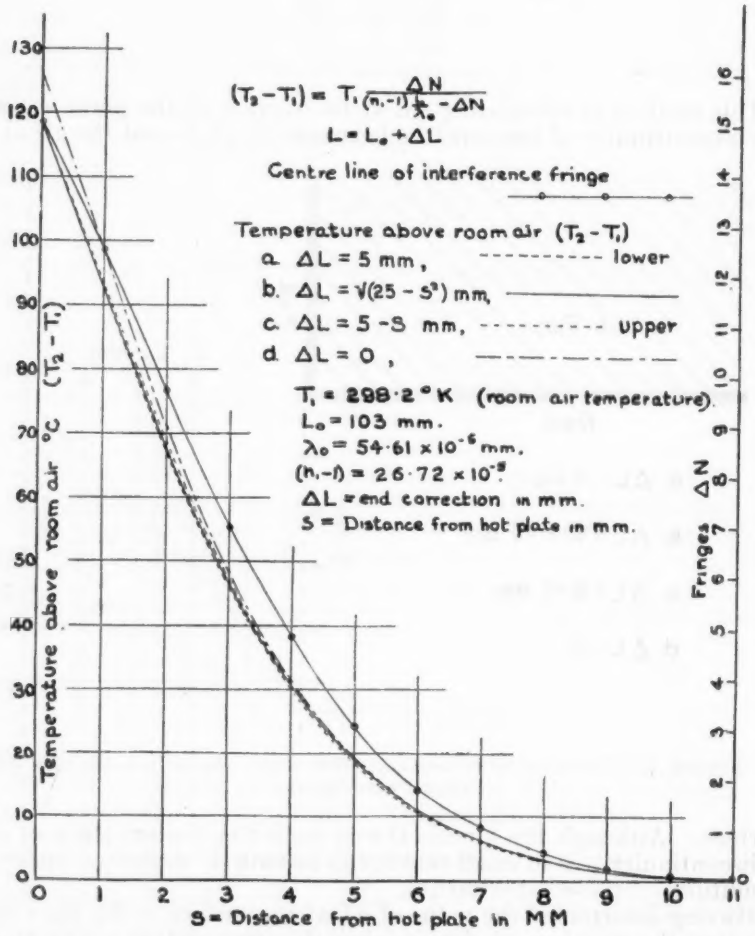

$(T_2-T_1) = T_1 \frac{\Delta N}{\frac{(n_0-1)}{\lambda_0} L - \Delta N}$
$L = L_0 + \Delta L$
Centre line of interference fringe
Temperature above room air (T_2-T_1)
a. $\Delta L = 5$ mm, lower
b. $\Delta L = \sqrt{(25-S^2)}$ mm,
c. $\Delta L = 5-S$ mm, upper
d. $\Delta L = 0$,
$T_1 = 298{\cdot}2$° K (room air temperature).
$L_0 = 103$ mm.
$\lambda_0 = 54{\cdot}61 \times 10^{-6}$ mm.
$(n_0-1) = 26{\cdot}72 \times 10^{-5}$
ΔL = end correction in mm.
S = Distance from hot plate in mm.
Temperature above room air °C (T_2-T_1)
Fringes ΔN
S = Distance from hot plate in MM

FIGURE 4.—*Variation of fringe shift and of temperature with distance from a hot plate, the latter corrected for end effect according to several assumptions*

Below the observed fringe displacement, four curves are shown which give the corresponding temperatures as calculated for four different assumptions for the end correction. This figure shows clearly the justification of the empirical choice of $\Delta L = \sqrt{25-S^2}$ as the end correction.

It is clear from this figure, as well as from equations (8) and (9) that the interference fringe does not represent the temperature line.

The difference, however, becomes much less as the total temperature rise becomes smaller.

3. EFFECTS OF ABERRATION

Another factor that needs to be considered is that not every ray through a given point in the focal plane has come over the same path in front of the hot surface. Some of the rays may have come through warmer, and some through colder regions of air. At a distance from the plate these effects are likely to balance each other and no appreciable error results. Furthermore, the effect can be reduced by using a small aperture in front of the camera lens. If a 3 mm aperture is used, with the focus set on one edge of the plate, the cone of light entering the lens from a point in the focal plane will have a diameter at the other edge of 0.55 mm.

At the surface of the plate the error will be greatest, and it may be shown that it will amount to the difference between the temperature of the plate and that at a distance of 0.12 mm on the assumption that all rays within the half cone are equally probable and that an average is taken of each ray over its full length across the plate. The above value also assumes perfect collimation of the set.

As even with the greatest care, errors due to collimation will occur, an aperture of 6 mm was used in the majority of the exposures. By this increase in aperture the time of exposure could be reduced to 6 seconds. With the 3 mm aperture an exposure of more than 20 seconds was required and many plates were spoiled by stray air currents which caused the fringes to move.

It will be noted that the purely empirical method used in making the end correction tends also to correct for small errors caused by aberration and imperfect collimation.

IV. VERTICAL HOT PLATE

1. EXPERIMENTAL RESULTS

Four photographs showing the fringe displacement in front of a vertical hot plate are shown in Figure 5. In each photograph the edge of the plate is seen at the extreme right. The straight part of the fringes at the left indicates room air temperatures. The hot plate is 210 mm high and 103 mm wide. In each case the center of the plate is shown at the bottom of the photograph. The temperature difference between room air and the hot plate is given with each figure. The room air temperature varied from 21.7° to 25.2° C., and was measured by a shielded thermocouple T shown in Figure 1. The plate temperature was measured by a thermocouple soldered to one edge of the plate. The photograph of the millimeter scale was obtained by a double exposure on one of the photographs of the fringes, all of which are enlarged to the same scale.

Figure 6 shows the effect of the total temperature rise on the relative temperature distribution. In the preliminary report [16] on this work, it was stated that the distribution was the same for all temperatures, any differences which occurred being ascribed to experimental error. Repeated measurements have since been made on the enlarged photo-

[16] Kennard, Phys. Rev., vol. 38, p. 1921, 1931.

graphs which indicate that there is a small but systematic effect as shown in the figure. In the terms of the film theory, the straight portions of the curves near the plate surface indicate that the temperature coefficient of film thickness is approximately -0.12 per cent per degree. Lines a', d', and d'' will be discussed later.

2. DISCUSSION OF FIGURE 6

No function has as yet been developed which represents the observed temperature distribution in front of a vertical hot plate. It

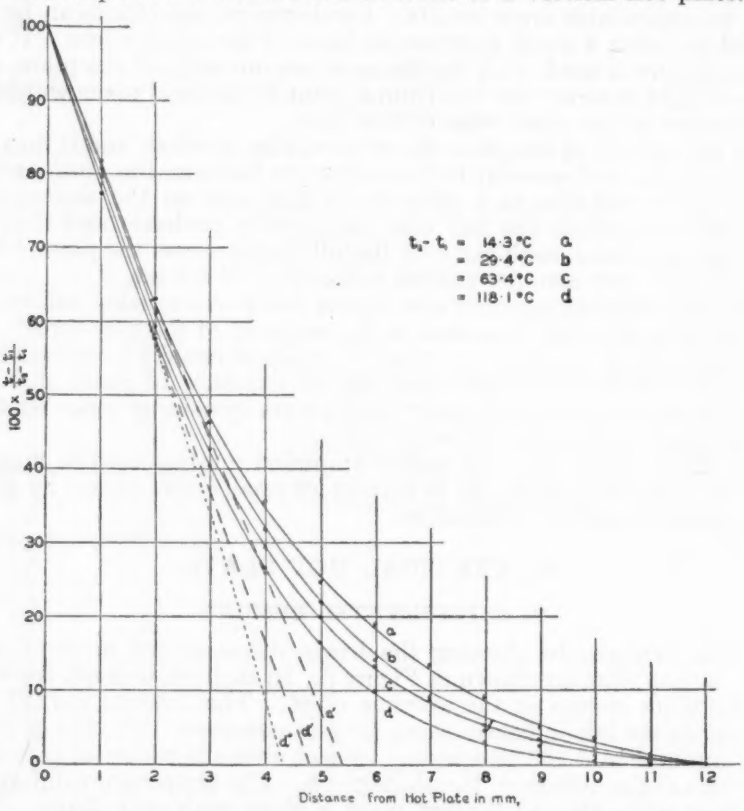


FIGURE 6.—*Effect of total temperature rise on relative temperature distribution for vertical plate*

will be noted that the curves in Figure 5 show no sharp change in slope or in curvature, and that the curves approach the room temperature line asymptotically. Whatever the above function may be, it seems evident from these curves that it is continuous both in its first and second derivatives.

These curves may be interpreted as follows: Near the surface the warm air rises parallel to the plate with very nearly stream line or laminar flow. In this region which includes 40 or 50 per cent of the

temperature drop the heat transfer closely approximates pure conduction. Cold air from a distance is drawn into this rising column of warm air. As the cold air approaches the plate it is heated either by pure conduction or by fine grained turbulence. The presence of large scale vortex turbulence is ruled out by the fact that the interference fringes remain sharp throughout the field over a six-second exposure. Fine grained turbulence, in which the vortices have a diameter of 1/10 mm or less, may exist and might account for the shape of the curves for the lower half of the temperature drop by the mixing of the warmer and colder air.

For the middle portion of a short plate as used in this experiment, the observed temperature distribution may be accounted for without the assumption of turbulence. For a long plate, at points far from the bottom the assumption of turbulence seems necessary to account for the fact that the convective heat transfer is practically independent of the height.

3. CALCULATION OF CONVECTIVE HEAT TRANSFER

From the temperature gradient at the surface of the plate, assuming pure conduction in this region one may calculate the rate of convective heat transfer per unit area.

$$Q = -K\frac{dT}{ds} \tag{15}$$

where K is the conductivity of the air taken at the plate temperature.

For a temperature rise of 118.1° C. with the plate at 143.3° C.

$$K = 0.000308 \text{ watt cm}^{-1} \text{ °C.}^{-1}$$

and

$$\frac{dT}{ds} = 246° \text{ C. cm}^{-1}$$

whence

$$Q = 0.0760 \text{ watt cm}^{-2}$$

For a temperature rise of 14.3° C. with the plate at 36.8° C.

$$K = 0.000246 \text{ watt cm}^{-1} \text{ °C.}^{-1}$$

and

$$\frac{dT}{ds} = 27° \text{ C. cm}^{-1}$$

whence

$$Q = 0.00666 \text{ watt cm}^{-2}$$

If we set $\frac{Q_1}{Q_2} = \left(\frac{\Delta t_1}{\Delta t_2}\right)^n$ we find $n = 1.17$ which is considerably less than the value 1.25 generally taken, but agrees very well with the value found by Griffith and Davis for short vertical cylinders. Their value, however, is for the total heat emitted, whereas the above value applies to the particular portion of the plate photographed.

V. HORIZONTAL CYLINDERS

1. EXPERIMENTAL RESULTS

Photographs were taken of the interference fringes about horizontal heated cylinders. Figure 7 shows a composite photograph about a cylinder 3 cm diameter and 10 cm long. The cylinder is made of two coaxial brass tubes with the heating coil between. The supports are vertical transite plates 3 mm thick which are inserted into the ends of the inner cylinder and extend 1½ cm beyond the end. A thermocouple, soldered to the back of the outer cylinder gives the surface temperature.

The photographs were taken in the order upper left, lower left, bottom, and top. The imperfect match between the top and the upper left photograph can be accounted for by a slight shift in the adjustment of the interferometer in the three hours necessary to complete the set. Such a change has no effect in plotting the temperature field as each photograph is taken as a unit.

In Figure 8 the isothermal lines have been drawn about the cylinder by connecting the points of equal fringe displacement. The correction for end effect was made by assuming that the fringe displacement at the surface corresponds to air having the temperature of the surface of the cylinder, with proportional correction for the lower temperatures. The outer line indicates the boundary of the region of heated air. Along this line the temperature is less than 0.3° C. above that of the room. From the fringes in Figure 7 it will be seen that the departure from room temperature is at first very gradual. The exact position of the outside boundary is therefore indefinite.

One may safely assume that at the surface of the cylinder the air flow is approximately laminar and that the heat is transferred by pure conduction. Under such conditions the heat flux will be directly proportional to the temperature gradient, which can be determined from the spacing of the isothermal lines. If we take the heat flux at the bottom as 100, we find from Figure 9 that it decreases uniformly to 70 at the side. This uniform decrease continues to about 45° from the top where the heat flux begins to drop off more rapidly, so that at the top it is only 10. However, the isothermals shown at the top of the cylinder are so far from the surface that it is not safe to assume laminar flow throughout this region. In case of turbulence the heat flux might be considerably greater than that indicated by the average temperature gradient over the distances involved.

In Figure 9*A* is shown a composite photograph of the fringes about a cylinder 1.27 cm diameter and 10 cm long. The cylinder is of brass tubing, having a 1 mm wall and is lined with asbestos paper which is held in place by the heating coil. The leads to the heating coil project a few millimeters beyond the cylinder and are then bent sharply to the right and serve as the support. The cylinder is open at both ends and the interference fringes are clearly seen through the hollow center. The surface temperature of the cylinder is determined by the thermocouple wires shown in the lower right of the photograph.

In Figure 10(*A*) are shown the isothermal lines about the above cylinder. They were determined as in Figure 8 by plotting the points of equal fringe shift. From the spacing of the isothermal lines

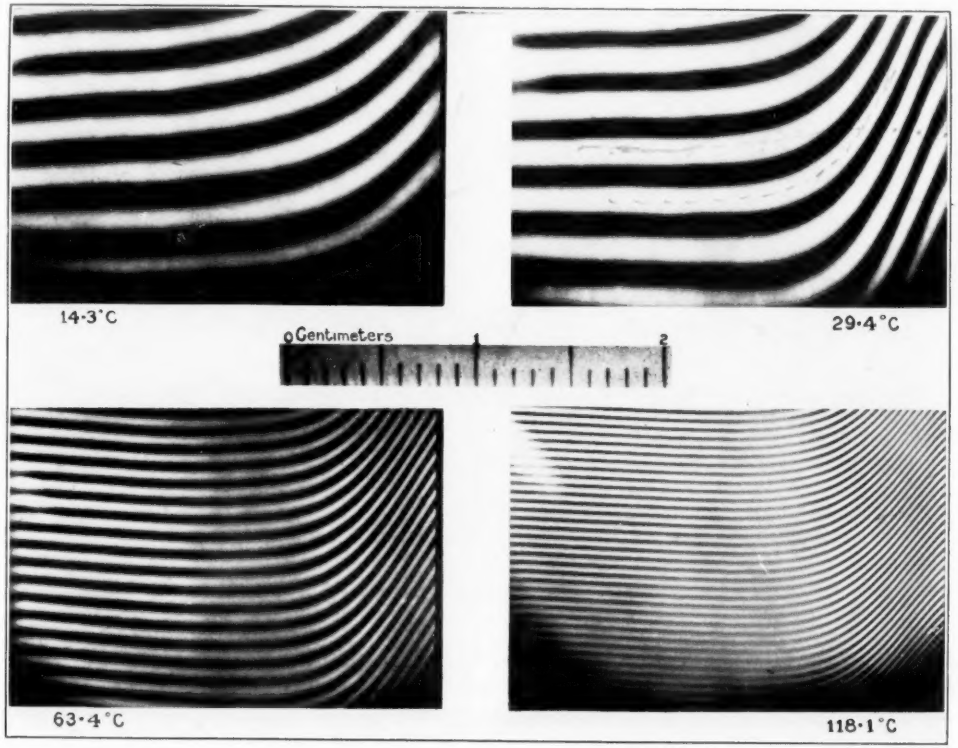


FIGURE 5.—*Fringes in front of a heated plate for the values of temperature rise indicated below each photograph*

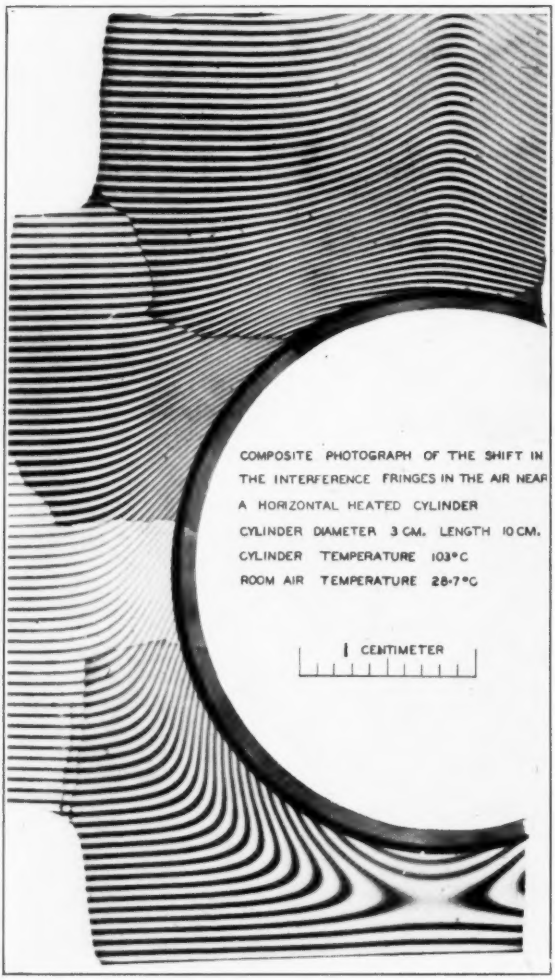

COMPOSITE PHOTOGRAPH OF THE SHIFT IN
THE INTERFERENCE FRINGES IN THE AIR NEAR
A HORIZONTAL HEATED CYLINDER
CYLINDER DIAMETER 3 CM. LENGTH 10 CM.
CYLINDER TEMPERATURE 103°C
ROOM AIR TEMPERATURE 28·7°C
1 CENTIMETER

FIGURE 7

near the cylinder the heat flux is found to decrease from 100 at the bottom, to 80 at the side, and to 20 at the top.

Figure 9(*B*) shows a photograph of the fringes about a cylinder 5 mm in diameter and 10 cm long. The walls are 1 mm thick and lined with alundum cement. A straight nichrome wire serves as both heating element and support. The thermocouple giving the surface temperature is shown at the right center with the heating and support

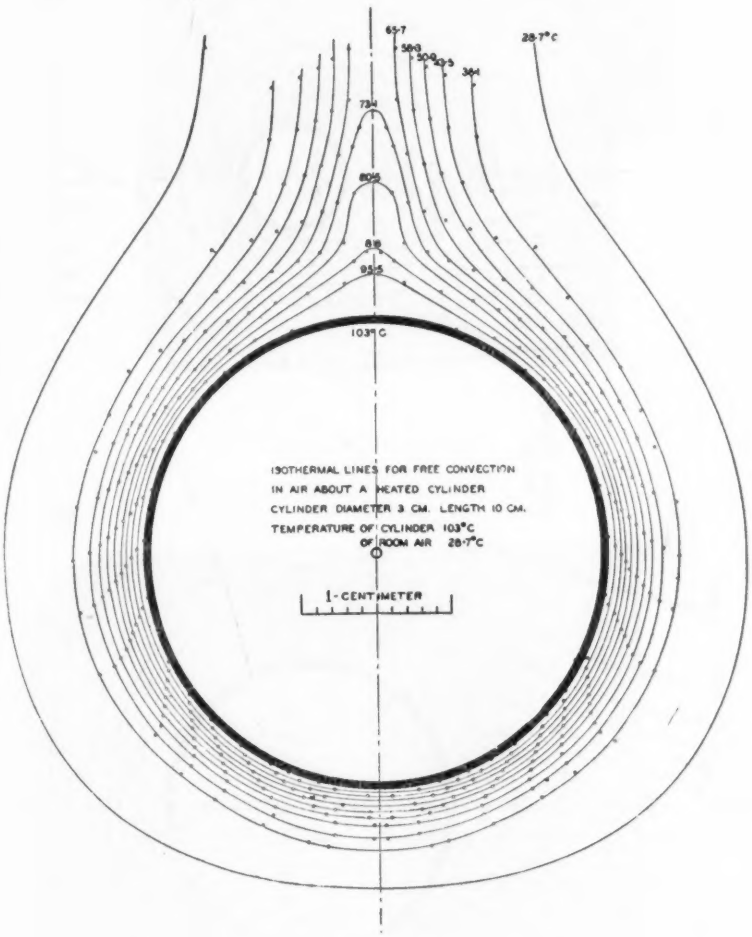
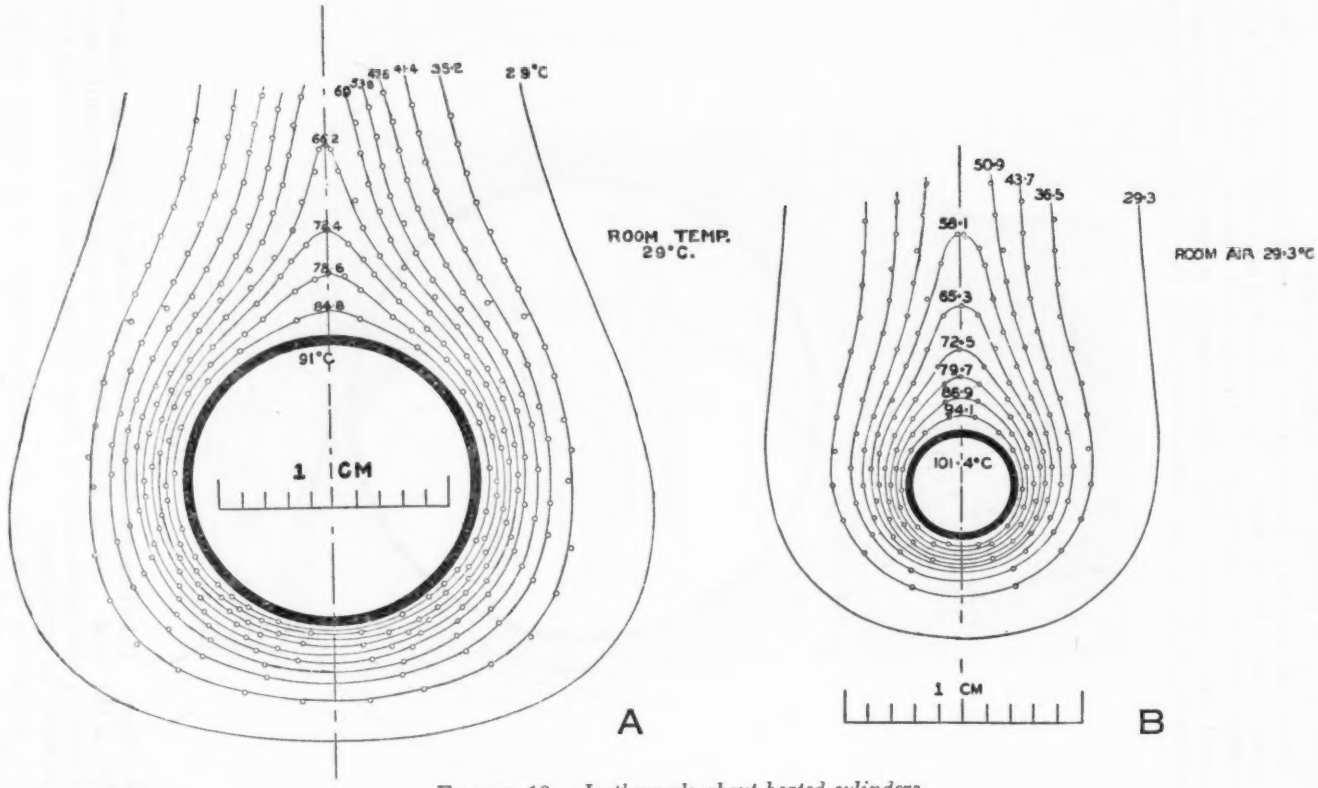


FIGURE 8

wire below. Interference fringes may be seen through the hollow center of the tube. As the hole is 100 mm long and only about 1 mm in diameter, the appearance of these fringes gives an idea of the collimation of the apparatus.

The isothermal lines for this cylinder are shown in Figure 10(*B*). From the spacing of the isothermals the heat flux is found to decrease from 100 at the bottom to approximately 90 at the side, and to 30 at the top.



A, diameter 1.27 cm
B, diameter 5 mm

FIGURE 10.—*Isothermals about heated cylinders*

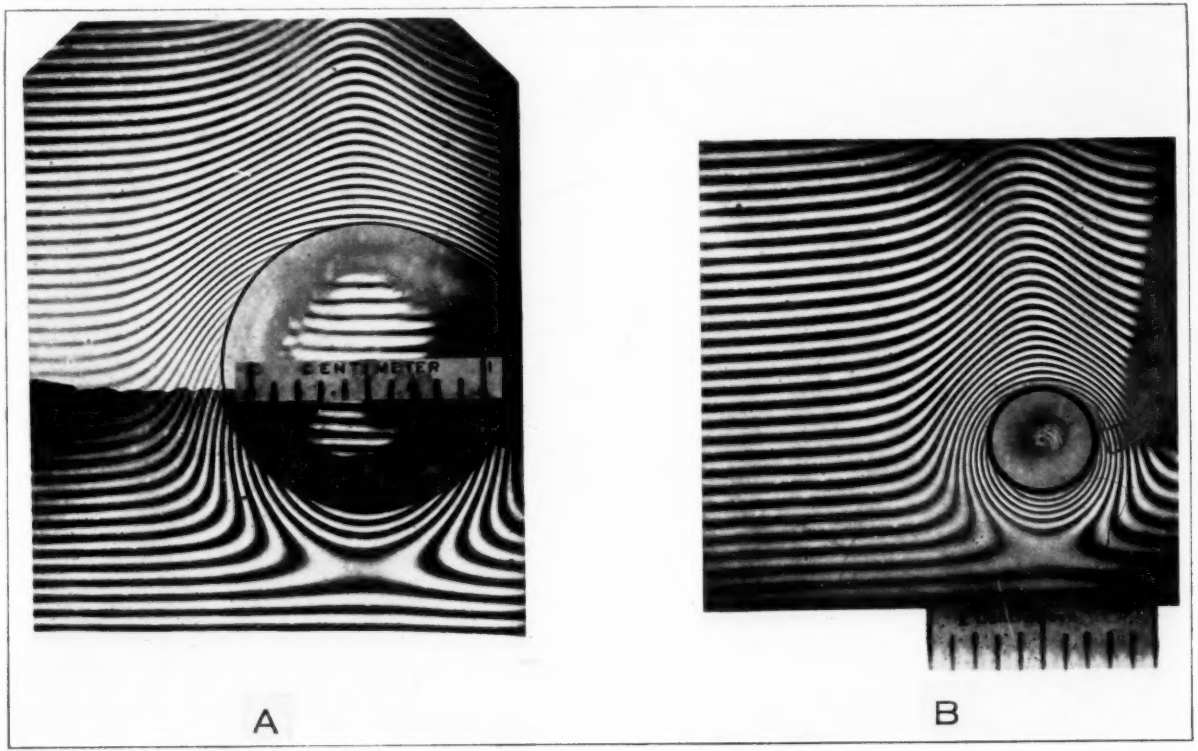


FIGURE 9.—*Fringes about heated cylinders*

A, Diameter 1.27 cm; *B*, diameter 5 mm.

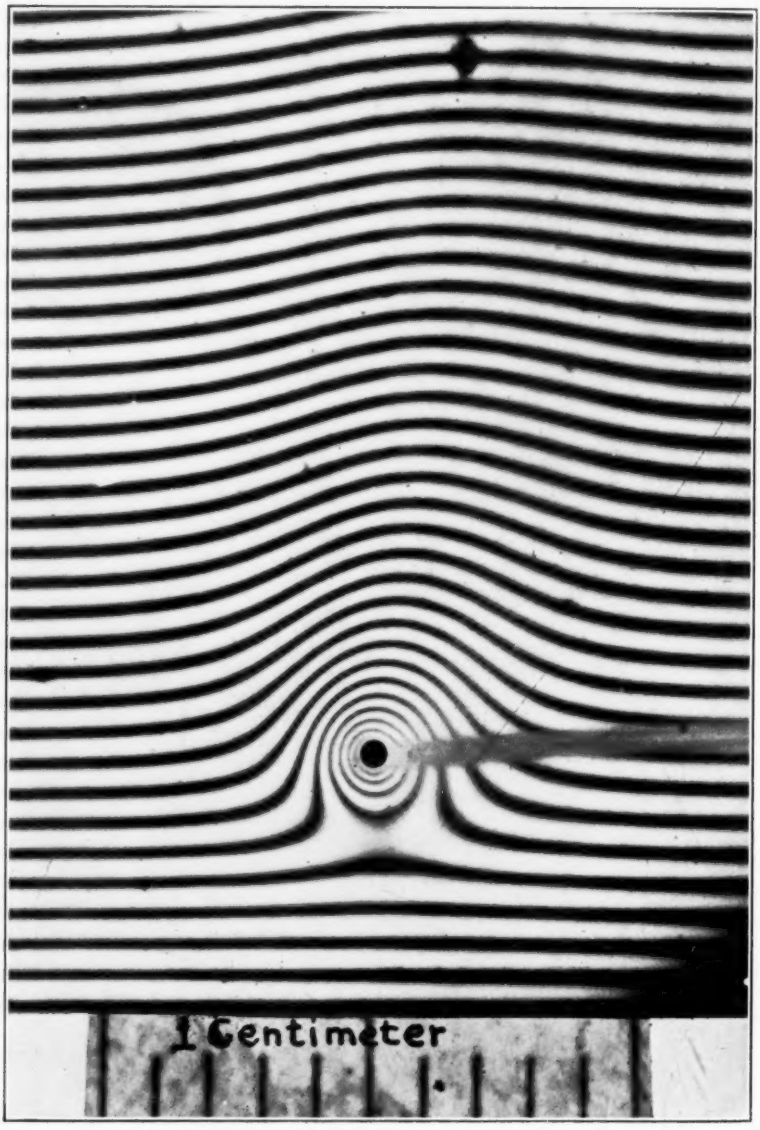


FIGURE 11.—*Fringes about a wire 0.4 mm in diameter*

In Figure 11 is shown a photograph of the fringes about a horizontal platinum wire 0.4 mm in diameter. The current and the potential drop were measured on a potentiometer and the temperature determined from the resistance. Potential leads were used so that the resistance measured was only that of the straight portion of the wire about which the fringes were photographed and did not include the leads. In order to throw the leads out of focus and to reduce the aberration error the fringes were brought to a focus at the middle of the wire.

The isothermal lines about this wire are shown in Figure 12. It was not possible to get as many points of equal fringe displacement as

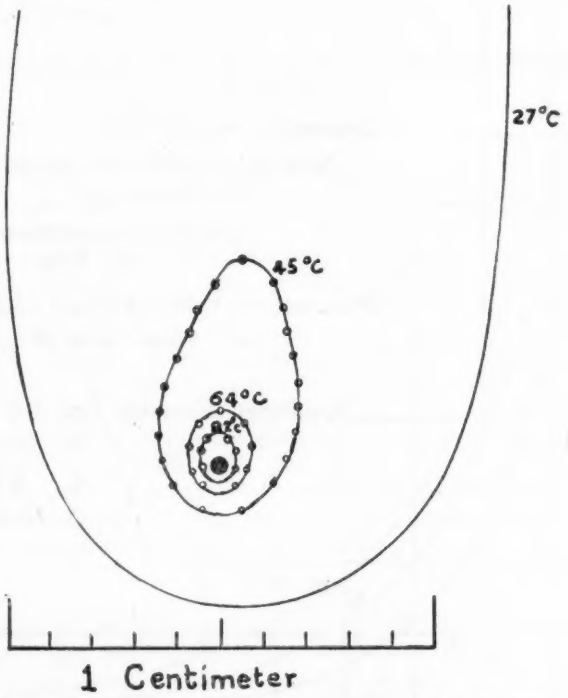


FIGURE 12.—*Isothermals about a wire 0.4 mm in diameter*

in the case of the other cylinders, and only four isothermals have been drawn. These are sufficient, however, to show that the heat flux changes approximately from 100 at the bottom to 90 at the side, and to 30 at the top.

Figure 13 gives the temperature distribution for the four cylinders in a horizontal plane containing the cylinder axis. The curves for the distribution in a vertical plane below the cylinders are similar to those in this figure but closer to the surface. It will be noted that the curves in Figure 13 show no evidence of discontinuity in slope or curvature.

2. DISCUSSION

The temperature distribution for radial heat conduction from a cylinder for constant heat flow may be expressed mathematically by

$$t = A - B \log r \tag{16}$$

where t is the temperature and r the distance from the center.

The constants A and B may be determined by inserting the observed values of t and r at the surface of the cylinder and at some other

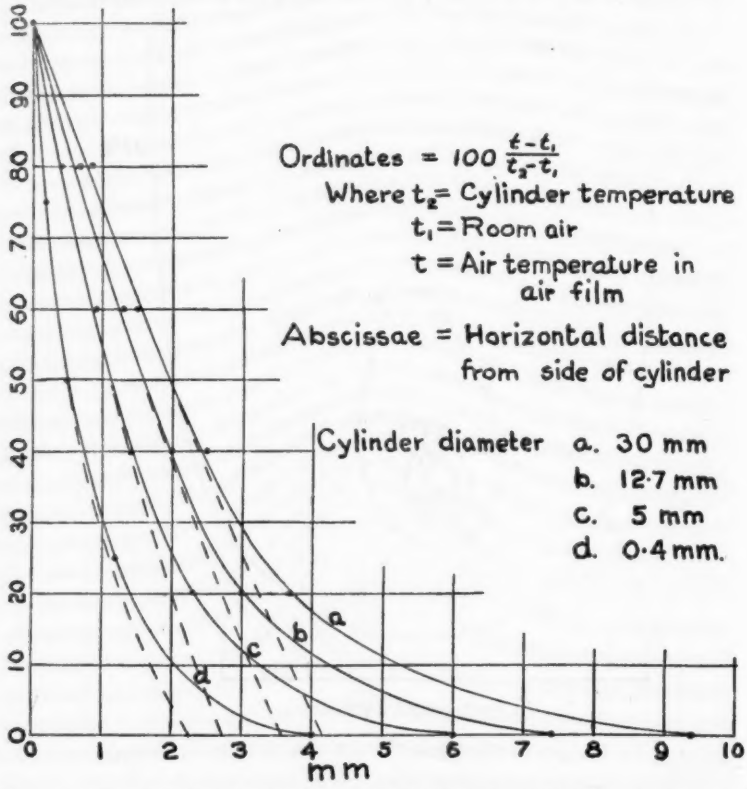


FIGURE 13.—*Relative temperature distribution for cylinders as measured experimentally compared with the film theory*

point for which t and r are known. If we take for t and r the room air temperature and the horizontal radius to the point at which this temperature is reached, the values for A and B so obtained will give a temperature distribution for pure conduction that corresponds only at the end points with that observed. If, however, the observed point for half the temperature drop is chosen, it is found that the temperature distribution as calculated for pure conduction coincides closely with that obtained from the fringe shift for the upper half of the temperature drop. For the lower half of the temperature drop there is a wide divergence. The broken lines in Figure 13 represent

the temperature distribution for pure conduction when fitted to the point of mean temperature drop as indicated above.

The curves in Figure 13 may be interpreted as were those for the vertical hot plate in Figure 6. That is, at the bottom and the sides of the cylinder, heat is transferred for the first half of the temperature drop under conditions closely approximating pure conduction. The temperature gradient then becomes much less than that called for by radial conduction. The change in temperature gradient may be accounted for by the presence of fine-grained turbulence, or by assuming that cold air is drawn in with laminar flow and heated.

No interpretation is offered of the temperature distribution at the top of these cylinders, as conditions with regard to turbulence in this region are not known.

VI. COMPARISON OF OBSERVED RESULTS WITH FILM THEORY

1. VERTICAL PLATE

It is of interest to contrast the temperature distribution as found from these experiments with that assumed by the film theory. In the case of the vertical hot plate the curve representing temperature distribution under the conditions assumed in the film theory would be very nearly a straight line, ending at room temperature at 4.3 mm from the plate.[17] This curve would be slightly convex upward because of the decrease in conductivity of the air with decrease in temperature, which would cause an increase in the temperature gradient at the lower temperatures. The dotted line d'' in Figure 5 shows the temperature distribution under the conditions assumed in the film theory, taking into consideration the change of thermal conductivity with temperature. The broken lines a' and d' are straight and indicate the temperature gradient at the surface. The wide departure of the observed temperature distribution from that assumed by the film theory is clearly seen in this figure.

2. CYLINDERS

A sketch of the conditions assumed to exist for heat transfer from cylinders as given by Rice [18] is reproduced in Figure 14. The temperature distribution under these assumptions will have radial symmetry and will, along any radius, be represented by curves similar to the broken lines in Figure 14. From the isothermal lines shown in Figures 8, 10(A), 10(B), and 12 it is certain that radial symmetry does not exist. There is also no evidence that the temperature distribution in any radial plane corresponds to the conditions of pure conduction through a film of limited thickness. At the bottom and sides of the cylinder the temperature distribution does, however, correspond to pure conduction for the upper half of the temperature drop.

It will be seen that the conditions implied by the film theory do not hold for free convection in air from a vertical hot plate nor from horizontal heated cylinders from 0.4 mm to 30 mm in diameter. It is not likely that these assumptions hold more closely under other

[17] See footnotes 8 and 9 p. 788.
[18] See footnote 5, p. 788.

conditions. Drew, Hogan, and McAdams [19] have shown the complete lack of radial symmetry of the heat flux in the case of forced convection in air from a pipe normal to the air stream. Griffith and Davis [20] show, for free convection from a vertical hot plate, that there is a variation of the temperature distribution with distance from the bottom of the plate. This variation is much more marked

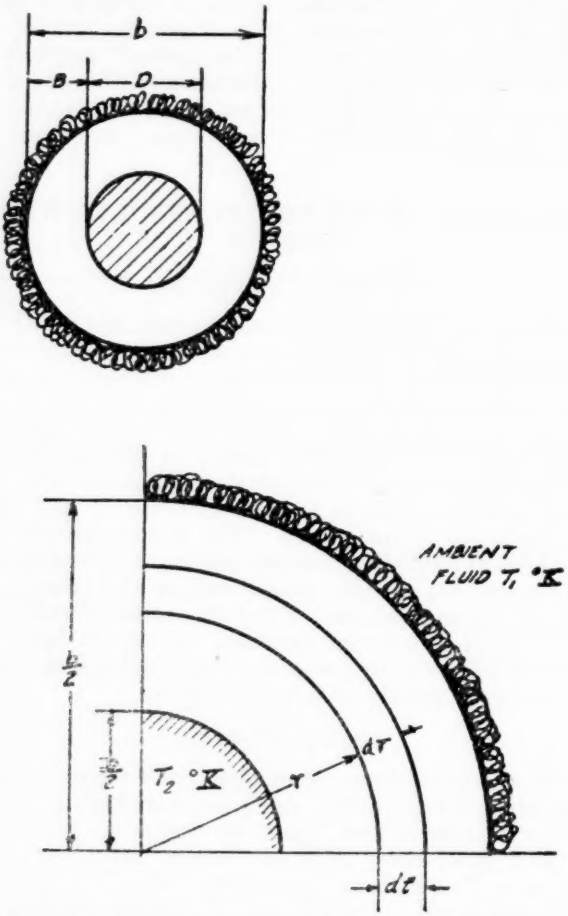


FIGURE 14.—*Film theory for cylinder, according to Rice*
(Reproduced from Trans. A. I. E. E., vol 42, p. 653, 1923.)

for forced convection from a hot plate as shown by Jürges [21] and Elias [22] The film theory permits no such variation.

As actually used [23] to calculate convective heat transfer, the film theory serves merely as a device by which experimental results may be correlated by means of dimensional analysis. Experimentally determined coefficients of heat transfer could serve the purpose equally

[19] Ind. Eng. Chem., vol. 23, p. 936, 1931.
[20] See footnote 10, p. 789.
[21] See footnote 11, p. 789.
[22] See footnote 13, p. 789.
[23] I. C. T., vol. 5, p. 234.

well, and not be open to the criticism of being based on a false physical assumption. The assumption of a film or any other device is not necessary for this purpose as indicated by the work of Fishenden and Saunders.[24]

VII. CONCLUSION

An apparatus has been devised by which the temperature of the air near heated surfaces may be determined without the use of any material thermometric device. This is accomplished by measuring the displacement of the fringes in a suitable interferometer. A series of photographs have been taken of the interference fringes near a heated vertical plate and about heated horizontal cylinders of different diameters. The results show that the temperature distribution does not conform to that assumed by the film theory.

The apparatus also makes it possible to determine the temperature gradient in the air at any point on the heated surface, thus making it possible to calculate the heat flux at that point. This has not been possible with any apparatus heretofore developed.

VIII. ACKNOWLEDGMENT

The writer wishes to acknowledge his indebtedness to H. C. Dickinson, who suggested the possibility of using the technic of interferometery to study the conditions in the fluid near a solid heated surface. He wishes also to thank M. S. Van Dusen for valuable suggestions in the interpretation of results.

The writer also wishes to make special acknowledgment of his indebtedness to the Johns-Manville Corporation, who made possible this investigation by the establishment at the Bureau of Standards of the L. B. McMillan Fellowship for fundamental studies in the transfer of heat between solids and fluids.

NOTE.—After the manuscript of this paper was completed, the paper by Hansen (Zeit für Tech. Phys. XII, 9, 1931) was received. Hansen describes the design and construction of an elaborate interferometer for use in work similar to that described here, and goes into the optical theory in detail. As concerns heat transfer he does not go beyond showing that it is possible to obtain photographs of the interference fringes displaced by a heated cylinder.

WASHINGTON, April 22, 1932.

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[24] See footnote 6, p. 788.

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